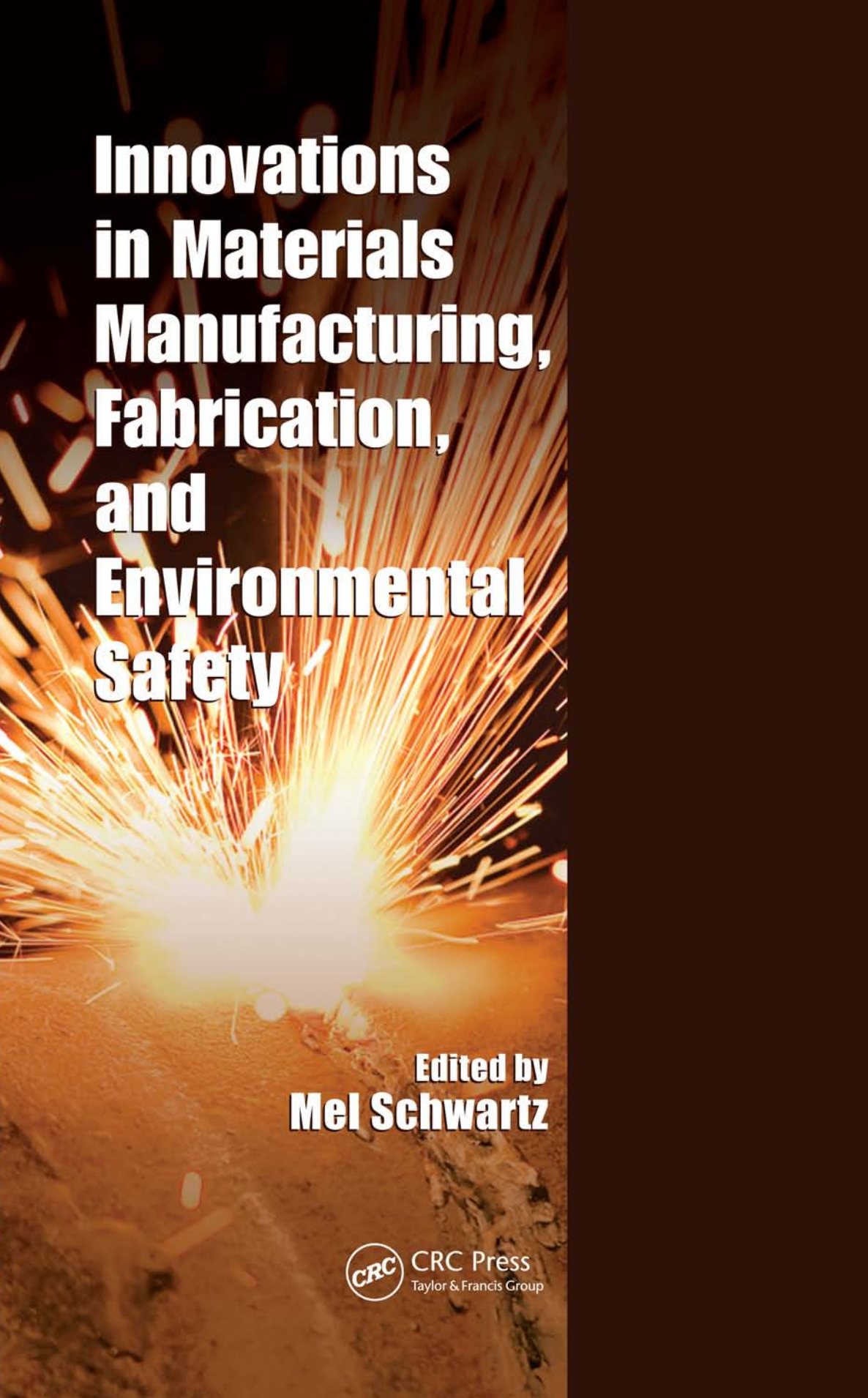




Innovations in Materials Manufacturing, Fabrication, and Environmental Safety

**Edited by
Mel Schwartz**



CRC Press
Taylor & Francis Group

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Taylor & Francis Group

Boca Raton London New York

CRC Press is an imprint of the
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CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

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Printed in the United States of America on acid-free paper
10 9 8 7 6 5 4 3 2 1

International Standard Book Number: 978-1-4200-8215-9 (Hardback)

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*To my family whose free-flowing love and encouragement have
endured for 40 years of my book publishing career.*

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Preface

Throughout industries, pressure for change now comes from all directions—technical, financial, environmental, political, and social. The roadmap for new and developing processes, technologies, and materials provides a vision that shows company-by-company efforts aren't enough—implementing such a vision requires extensive value/chain collaboration and public/private partnerships. To ensure success in a highly competitive environment, the government must be part of the business strategy, especially long-term funding of research and development. Technical societies could also be a prime mover and act as a catalyst/facilitator at times.

In the research and development of new materials or variations of new processes, the word “innovation” for the scientist means something altogether different from the interpretation by the general public. According to Margaret W. Hunt, editor of *Advanced Materials & Processes* magazine, “Innovation is really a state of mind, a fundamental attitude of willingness to try new and sometimes radically different approaches to problems.” This is the state of mind of the engineers who help drive the innovations that prime the U.S. economy. No one can predict the wonders that will become commonplace in the future, but it is safe to predict that they will be based on unseen developments.

For the general public, innovation brings to mind such products as cell phones and laptop computers, not advanced materials and process technologies. However, the inventors of these devices know that without advanced materials, joining methods, processing, and testing technologies, clunky telephones and typewriters would still be the norm, not to mention heavy and inefficient automobiles. These innovations that save money and reduce costs are often hidden from the ultimate consumer, who might not realize that the improved mileage in a new car is partially due to a metal diecast or molded plastic part that weighs less, that better safety is provided by stronger steel, and that new coating methods make the car look better and last longer. These things are invisible and the engineers who design and develop them often do not receive the credit they deserve.

A roadmap that was created in 1998 to identify the robotics and intelligent machine (RIM) goals by the year 2020 is now in place. This national initiative called for focusing and strengthening research in intelligent systems to strengthen the entire industry—currently U.S. companies lead the world in sensory devices and algorithms. Intelligent machines are advanced sensory devices to collect information about their environment and use sophisticated algorithms to respond to the information. This RIM science will benefit industry and society.

Intelligent machines can provide value to companies in all segments of manufacturing. An important question to ask is: What can RIM help you do better? For example, the high-value consumer electronics manufacturers want intelligent production systems that can rapidly and easily accommodate new product lines; they want intelligent systems to ensure the manufacturability of a product line and autonomously reprogram themselves when a new design is introduced. The welding industry wants an intelligent machine that will result in a repeatable, high-quality, structurally reliable weldment.

Many of the manufacturing processes described in this book can, and likely will, benefit from the incorporation of an intelligent machine into the processing and fabrication cycle. For example, a project at the Idaho National Engineering & Environmental Laboratory (INEEL) currently involves intelligent welding machines that incorporate both knowledge of welding physics and empirical learning capabilities. Currently, welding is considered as an industrial art based on a welder's manual skills or very simple duplication of these skills by an automatic (but dumb) machine. A typical approach to a machine control problem is to have a central body of intelligence (and control) in the machine. However, researchers at INEEL have developed a conceptual design of a machine using distributed learning and intelligence. The design is loosely based on biological models of social insects. For example, in an ant colony each ant functions according to local rules of behavior. Thus methods of learning and behavior modification have been developed that ensure global stability and optimization of the total machine. Researchers believe a qualitative understanding of the relationships between local costs and global subcosts can be used to develop future models for a welding process, as well as in more traditional control systems for welding processes.

In this 21st century, there are numerous challenges that are being overcome and in some instances have been overcome. Increased emphasis has been put on new materials, new fuels and propulsion technologies, advanced manufacturing, and predictive engineering that will put tremendous demands on our educational infrastructure and necessitate changes in curricula. Various industrial learning centers have been actively engaged during the past 10 years with design-oriented and engineering schools, industry scientists and engineers who work with materials, and advanced processes in activities including seminars, workshops, forums, and national conferences.

The initiatives mentioned here require steadfast commitment to long-term research and development, advocacy, and communication. Individual and corporate participation is, of course, critical.

This book will discuss environmental issues and safety in regard to processes and processing. In fact, all products manufactured need energy for material and production. Professor Timothy G. Gutowski, Faculty of Mechanical Energy at MIT, has received a grant from the National Science Foundation (NSF) to conduct research into the energy use of manufacturing processes of materials. "Manufacturing processes can be thought of as

products with a huge energy appetite,” Gutowski says. “These processes contribute to global warming, but are not visible to the public, unlike gas-guzzling SUVs or images of melting polar ice caps.” Many people are not aware of the energy requirement for a lot of manufacturing processes, claims Gutowski. For example, the whole of the Western composites industry should be concerned. Upcoming economies such as China, India, Korea, and Malaysia are rapidly developing composite technologies and production processing.

Composites and energy could well be the criteria for future success in public transport. The subject of composites and energy is strongly related to population growth, mobility, and transport systems. Countries that have new economies are less hindered by rules, regulations, laws, and standards, and they are able to start from a different playing field. These countries have the best of both worlds—their own low cost of manufacturing and a highly educated population, and the loan of the often rusted technology know-how from Western countries. Southeast Asia is going to be in strong competition with the Western world. This should be a major concern to industry in the future. However, being different may be the only way the Western world of industries can sustain, by being one step ahead of the rest of the world and focus on what is the most important area for future growth and development; that is, resin transfer molding (RTM) composites and energy.

Speaking about energy, fresh research out of Yale University concludes that the energy required to produce nickel-containing, austenitic stainless steel from scrap is less than a third of the energy used to produce stainless steel from virgin sources. As an additional environmental bonus, recycling produces just 30% of the CO₂ emissions. Already one of the most recycled materials in the world, stainless steel could, theoretically, be made entirely from scrap if there weren't serious limitations on the availability of this material. Ironically, one of the main benefits of the material—its durability—limits its recycling potential: stainless steel structures and products tend to last a long, long time.

Current recycling operations reduce primary energy use by about 33% and CO₂ by 32% compared with production from virgin sources alone. But if stainless steel were to be produced solely from scrap (a merely hypothetical scenario), about 67% of the energy could be saved and CO₂ emissions cut by 70%.

“It confirms common sense,” says Barbara Reck, a research associate at the School of Forestry and Environmental Studies at Yale. “The biggest energy use is in the mining and smelting phase, and you don't have to go through this phase using scrap. But now calculations have shown this systematically and the hypothesis has been confirmed.” These findings have implications for the thousands of end-users of nickel-containing stainless steels.

In today's environmentally conscientious marketplace, customers want assurance that the products they buy will not contribute to climate change. They prefer to contribute to a sustainable world. Today products are

advertised as being made of materials that have been validated, by one association or another, as safe for the environment. For example, in Northbrook, Illinois, a U.S.-based Crate and Barrel reports that its sofas have wood frames “certified by the Sustainable Forestry Initiative” and that they are “guaranteed for life.” What’s more, its cushions are “created with revolutionary, bio-based materials that are environmentally renewable.” The advertisement concludes: “Sustainability is a beautiful thing.”

The same can be said of products made of nickel-containing stainless steel. It is one of the world’s most recycled materials. Austenitic stainless steel products are all around us. Our kitchen appliances and sinks are made of it, we cook our meals in it, we eat our meals with it, the material has been available for less than 100 years, and is increasingly recycled. More than 80% of all products made of austenitic stainless steel are recycled at the end of their useful life. That has significance for the environment and sustainability. It means less energy is needed and less CO₂ emitted in the manufacture of austenitic stainless steel than in the past, when virgin material was all that was available. As more scrap becomes available, the need for virgin material declines and the carbon footprint left by a ton of austenitic stainless steel becomes smaller. The production of austenitic stainless steel is more sustainable than ever.

Fabricators and original equipment manufacturers (OEMs) must address health, safety, and environmental concerns. Infusion processing technologies especially must maintain a safe workplace including periodic training, adherence to detailed handling procedures, maintenance of current toxicity information, use of protective equipment (gloves, aprons, dust-control systems, and respirators), and development of company monitoring policies. Both suppliers and OEMs are working to reduce emissions of highly volatile organic compounds (VOCs) by reformulating resins and prepregs (pre-impregnated) and switching to water-dispensable cleaning agents.

So where does all this lead? Advances in materials technology and the convergence of materials, information, and miniaturization will drive less resource intensity, more complexity, and smart products. Older, established technologies will continue sideways development into new markets and applications. Innovations such as nanotechnologies, portable energy sources, multifuel products, miniaturization, and customizable intelligent materials will grow.

But how do we cope with these challenges and the opportunities that result?

We put the spotlight on innovation of new and exciting processing techniques, methods, and fabrication technologies developing the next business models, not only on new products, processes, and services within your own company. Identify novel segments and geographies, quickly spot new competitors and partners, and establish global positions quickly through acquisitions, alliances, and licensing. In addition, we must manage strategic risk—not just operational risk or political risk. Speed, flexibility, market

knowledge, effective alliances and acquisitions, and innovation will be critical success factors required to win in an environment driven by these mega trends.

In conclusion, we have before us opportunities and huge challenges. They are coming at us simultaneously ... we have no option to take them in sequence. We must play two hands.

Mel Schwartz

Editor

Mel Schwartz has degrees in metallurgy and engineering management and has studied law, metallurgical engineering, and education. His professional experience extends over 51 years serving as a metallurgist in the U.S. Bureau of Mines; metallurgist and producibility engineer, U.S. Chemical Corps; technical manufacturing manager, chief R&D Lab, research manufacturing engineering, and senior staff engineer, Martin-Marietta Corporation for 16 years; program director, manager and director of manufacturing for R&D, and chief metals researcher, Rohr Corp for 8 years; staff engineer and specification specialist, chief metals and metals processes, and manager of manufacturing technology, Sikorsky Aircraft for 21 years. While retired Mel has been a consultant for many industrial and commercial companies including Intel and Foster Wheeler, and was former editor for *SAMPE Journal of Advanced Materials*.

Mel's professional awards and honors include Inventor Achievement Awards and Inventor of the Year at Martin-Marietta; C. Adams Award & Lecture and R.D. Thomas Memorial Award from AWS; first recipient of the G. Lubin Award and an elected Fellow from SAMPE; an elected Fellow and Engineer of the Year in CT from ASM; and Jud Hall Award from SME.

Mel's other professional activities involve his appointment to ASM Technical Committees (Joining, Composites and Technical Books; Ceramics); manuscript board of review, *Journal of Metals Engineering* as peer reviewer; the Institute of Metals as peer reviewer as well as *Welding Journal*; U.S. Leader of IIW (International Institute of Welding) Commission I (Brazing & Related Processes) for 20 years and leader of IIW Commission IV (Electron Beam/Laser and Other Specialized Processes) for 18 years.

Mel's considerable patent activity has resulted in the issuance of five patents, especially aluminum dip brazing paste commercially sold as Alumibraze.

Mel has authored 17 books and over 100 technical papers and articles. Internationally known as a lecturer in Europe, the Far East and Canada, Mel has taught in U.S. colleges (San Diego State, Yale University), ASM Institutes, McGraw-Hill Seminars, and in-house company courses.

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Plasma Brazing

Dr.- Ing. Carolin Radscheit

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Why Plasma Brazing?

In the last 20 years, the weight of vehicles has been steadily increasing. This tendency can be applied to all makes and models of vehicles. The Volkswagen Golf I automobile was made from 1974 until 1983 and weighed only 870 kg, whereas the Golf 5 that started production in 2004 weighed about 1200 kg. This increase in weight is largely due to two factors:

- The increase in components concerning the safety of the occupants and the environment, for example, curtain and side airbags, antilock braking systems, belt tensioners, catalytic converters, and so on.
- The increase in components that increased driving comfort: electric windows, electrically operated sunroofs, power steering, air conditioning, and so on. For example, a maximum of five electric motors and control units were installed in the Golf 3 (from November 1991 until May 1997), whereas the Golf 5 possesses 25–30 such units with optimal equipment.

Parallel to this development, the construction of vehicles was changed so that safety could be provided through stable passenger compartments and consequently, the thickness of the body sheet metal was reduced. Most body panels today are thinner than 1.0 mm. Galvanization provides corrosion protection, which helps maintain the vehicle, its value, and enables

the vehicle manufacturer, Volkswagen, to offer guarantees against rust perforation.

Another development was the influence of joining techniques in body construction. Previous welding procedures have caused spattering on galvanized metal, and if the sheet metal is thin, there is a danger that it will be burn-through. As a result, new or modified joining methods were needed and required development.

Several brazing methods have been examined and developments have produced several new techniques. Three of these methods appear to have promise; however, the third method is the most applicable and is covered in this chapter.

The first process that was examined was laser beam brazing, which is suited for producing visually demanding and completely splatter-free seams. Therefore, this process has been used for outer surface joints, the boot lid (trunk) or hatch, and roof/side panel joints in autos. However, this process depends on maintaining small gaps ($g < 1.0$ mm), and can only be used in automated applications and also requires safety measures specific to laser beams.

The second method that was examined was MIG brazing (gas metal brazing), a metal inert gas process in which a copper-containing filler metal was used as a brazing material and is well suited for joining thin galvanized sheet metal. This process or ability to fill gaps well is especially advantageous when used with robots. However, this process is not splatter free and consequently has limited use for outer body surfaces. The splatter must be removed by grinding.

The third method and the subject of this chapter is plasma brazing, which offers an excellent compromise between the previous two modern brazing methods. Plasma brazing is very well suited for joining thin galvanized sheet metal, produces a narrow, visually appealing, and completely splatter-free seams and therefore has been used primarily on the outer body surfaces of autos. Plasma brazing can be performed manually as well as robotically and requires the same safety precautions as inert gas shielded welding.

How Plasma Brazing Works

A schematic diagram of the plasma brazing torch is shown in Figure 1.1. A plasma brazing machine consists of a plasma torch, a power source, a filler material wire feed, gas feed and, if required, a seam guide sensor, Figure 1.2. Plasma brazing is the equivalent of plasma welding with nonconducting filler wire. Just as with other welding and brazing processes with a side-feed

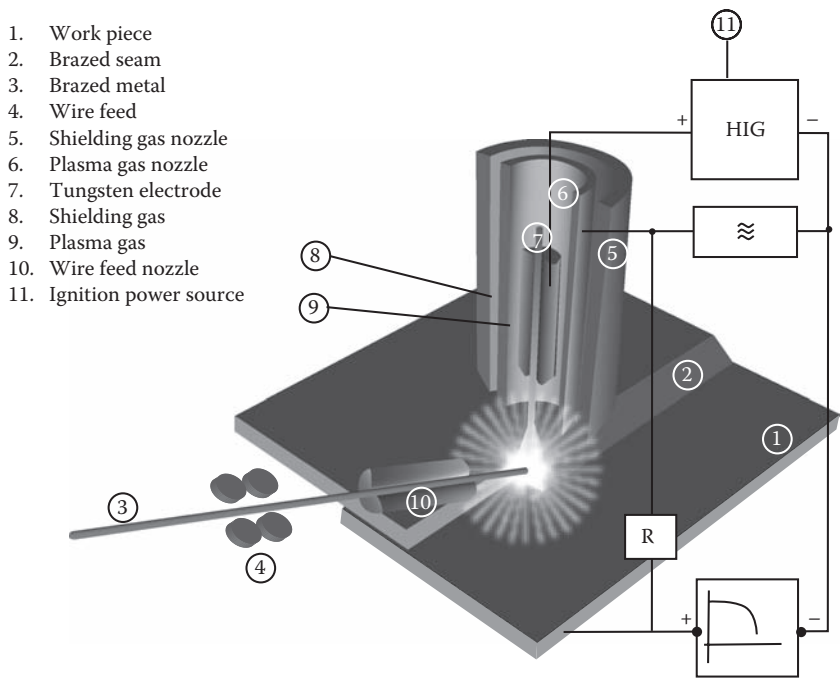


FIGURE 1.1
Schematic of a plasma brazing torch. (Courtesy of Fa. MIG-WELD, Landau Isar, Germany.)

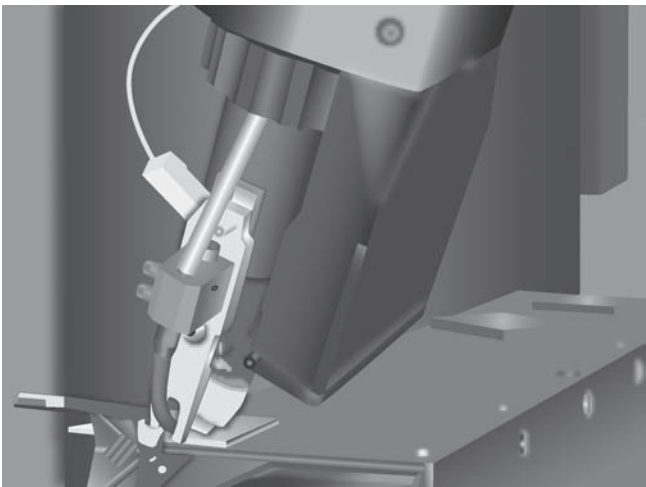


FIGURE 1.2
Plasma brazing head, including braze wire supply, brazing torch, and seam tracking sensor. (Courtesy of IGM-Robotersysteme, Wiener Neudorf, Austria.)

of wire, the accessibility of the torch is limited and in robotic applications, there is one degree of freedom less than with MIG brazing. Just as in laser or MIG brazing, a copper-based filler material has been used successfully in plasma brazing.

As can be seen in the diagram in Figure 1.1, plasma brazing requires two power sources: an ignition power source and a plasma power source with dropping power source characteristics. Actually, only manual procedures have this characteristic. Through the use of a seam guide sensor or reproducible work piece and gap size, however, this process can be used without any problems in robot-guided procedures. There are a number of variations of this new process, in part still in the developmental stages:

- Plasma brazing with only one inert gas and without an ignition power source
- Plasma brazing with conductive filler material wire
- Plasma brazing with brazing powder
- Plasma torch with central wire feed.

The plasma arc is restricted by the plasma gas and has an opening angle of only about 7° [1]. Therefore, the delivery of energy is very concentrated and the thermal efficiency is high.

Degree of efficiency	Plasma brazing	73 80%
For comparison [2]:	TIG	ca. 30%

The results reflect both a high fusion efficiency of the filler material and a low thermal influence on the work piece. The separate selection of wire feed and arc current strength in plasma brazing creates the possibility, for example, of performing repair brazing by remelting the existing material without needing to feed more wire [3].

What Plasma Brazing is Capable of Doing

Plasma brazing is primarily used to join coated, unalloyed or low-alloyed, deep-drawn sheet steel less than 1.5 mm thick. Plasma brazing of aluminum is under development. Sheet metal up to 15 µm galvanization can generally be joined without trouble. If, for example, hot galvanized or individual hot zinc dipped parts with thicker galvanized layers are used, a subsequent examination should be performed. Even sheet metal with organic layers (on zinc) can be joined with plasma brazing.

Combinations of material	ASTM A620-1008, 1.0 mm	ASTM A620-1008, 1.5 mm	H 180 B, 0.8 mm	H 220 P, 1.0 mm	H 220 P, 2.0 mm	H 260 LA, 1.0 mm	H 260 LA, 1.2 mm	H 260 LA, 2.0 mm	H 340 LA, 1.5 mm
ASTM A620-1008, 1.0 mm	X	X	X	X	X	X	X	X	X
ASTM A620-1008, 1.5 mm	X		X	X					
H 180 B, 0.8 mm	X	X	X	X	X	X	X	X	X
H 220 P, 1.0 mm	X	X	X	X	X	X	X	X	X
H 220 P, 2.0 mm	X		X	X		X			
H 260 LA, 1.0 mm	X		X	X	X	X	X	X	X
H 260 LA, 1.2 mm	X		X	X		X			
H 260 LA, 2.0 mm	X		X	X		X			
H 340 LA, 1.5 mm	X		X	X		X			

FIGURE 1.3

Brazed filler metal. Combinations of material and their suitability for plasma brazing (X), tensile shear test, R-CuSi-A (AWS/ASME).

The strength of the brazed joint depends on the filler metal used, the strength of the basic material used and the thickness of the material, and should be determined in individual cases, Figure 1.3. Currently, standardized copper-based brazing filler metal as well as nonstandardized copper-based brazing filler metal and welding wire have been used in plasma brazing. In car manufacturing, standard brazing filler metal R-CuSi-A (AWS/ASME, material number 2.1461) has proven to be an excellent and acceptable material of choice. This filler metal has been used in the form of wire, generally with diameters between 0.8 mm and 1.2 mm. Other available forms that have been used include powder, paste, cored wire, and solid, and cored wire with square or rectangular cross sections.

The surfaces of all work pieces and filler metal wire should be grease-free. Generally, welding argon Ar has been used as a shielding and plasma gas. The attainable brazing speed depends on the contours of the parts to be joined and, for a manual operation is about $v_B = 0.5 + 0.7$ m/min and for automatic operation, from about 7 m/min to about 1.0 m/min for $v_B = 0.3$ [2]. The holding fixture is crucial for the quality of brazing. The parts should be clamped close to the edge so that the parts cannot move during the brazing process. Gap widths of 0 is less than or equal to gap and is less than or equal to $1.5 t_{\min}$ and has produced good results.

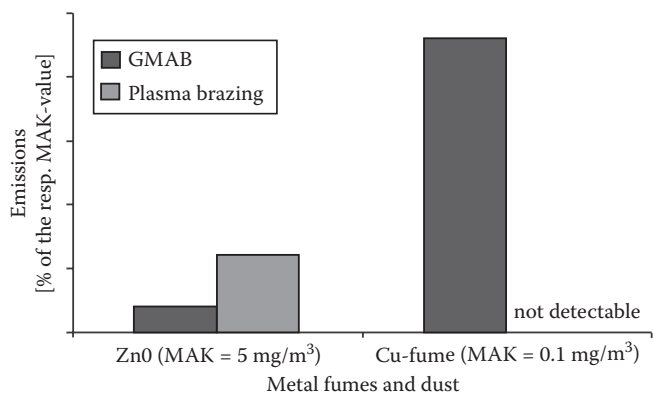


FIGURE 1.4
Comparison of emissions, GMAB versus plasma brazing, MAK = maximum work environment concentration.



FIGURE 1.5
Manual plasma brazing, carried out at the sidewall of a 31-Lupo vehicle.

A further characteristic of plasma brazing is that, in comparison to MIG brazing, there are no measurable Cu emissions, Figure 1.4. A few examples demonstrate the possible uses of plasma brazing. Manual plasma brazing is shown in Figure 1.5, which is appropriate for a small series of parts or prototype construction. Because the process is splatter free, it is also possible to make seams directly next to threads, Figure 1.6. In Figure 1.7, a robot-guided implementation series can be seen. The roof channel drain of the Volkswagen

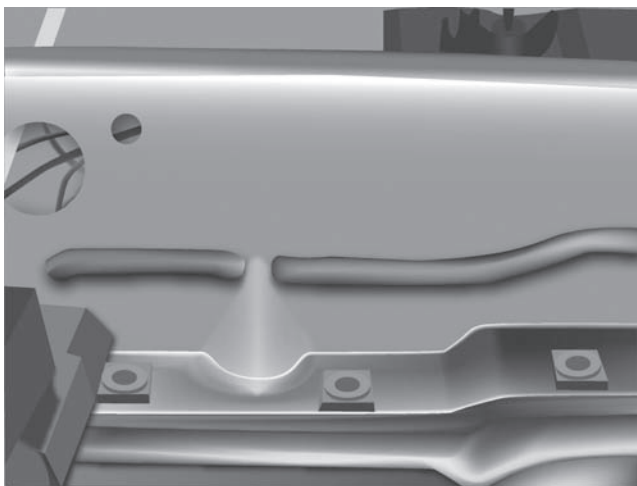


FIGURE 1.6
Plasma brazing at the pivot reinforcement. (Courtesy of VA-Tech, Linz, Austria.)

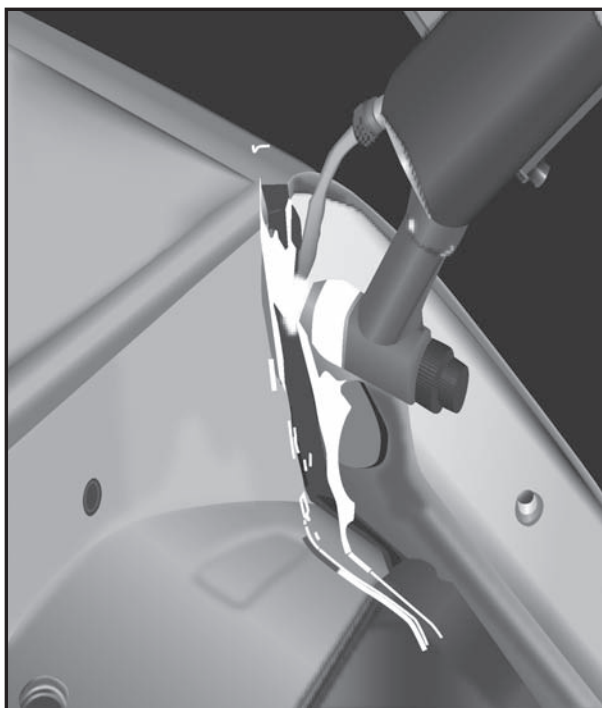


FIGURE 1.7
Robot guided plasma brazing at the car body of a GOLF 4 Volkswagen.

Golf 4 is welded with the aid of a seam sensor. Plasma brazing was chosen for this application because seams on the outside of the body would not require further work (grinding) [3,4].

Expected Developments, Future Potential, and Conclusions

Plasma brazing is appropriate on the exterior of the body of a vehicle. It is ideal for seams, which should not require further work but nevertheless must meet stringent visual standards. Currently, seams having these requirements are also made with laser brazing. Therefore, plasma brazing offers a possible alternative to the very elaborate and expensive laser process. Because plasma brazing is still a rather new process, some questions remain to be answered, for example:

- Do plasma brazers require special training?
- Will the process be classified as a welding or a brazing process in the standardization?

Results expected in the future from research and development include:

- Plasma brazing of aluminum, magnesium, and mixed combinations: Al-Mg or Al-Steel.
- Materials including filler metal specially adapted to this process as well as coating material.
- Robot-operated welding torches that fulfill the requirements of industrial series production.

In conclusion, plasma brazing can be characterized as a process, which is not a comprehensive production process but a process for special tasks at which other welding and brazing procedures fail. The uses, until now, also demonstrate the great potential for plasma brazing, the possibilities of which are far from exhausted.

Acknowledgments

I would like to express our gratitude to Mr. Stefan Lindenmayer and to Mr. Uwe Lahrman for their help.

References

1. Eichhorn, F. *Schweiss Technische Fertigungsverfahren*, Düsseldorf, Germany: VDI-Verlag, 1983, ISBN 3-18-400603-4.
2. Kallabis, M. (2003) Einsatz der Plasmatron-Technologie im Karosserie- und Anlagenbau, http://www.auscartec.com/news/powerslave,id,33,nodeid,89,_language,de.html
3. N.N. Lichtbogenlen Grundlagen, Verfahren, Anforderungen an die Anlagen-technik Merkblatt DVS 0938-1, Düsseldorf, Germany: DVS-Verlag, 2001.
4. N.N. Lichtbogenlen Anwendungshinweise Merkblatt DVS 0938-2, Düsseldorf, Germany: DVS-Verlag, 2004.

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Adhesive Bonding

Mel Schwartz

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Introduction and Brief History

Adhesive bonding as a joining technology was utilized in ancient times using natural materials. The first known application of adhesive in a structural application was the use of bitumen about 36,000 years ago [1] to bond wooden tool handles to flint stone. Various adhesive materials of animal or vegetable origin were used in ancient Egypt 3,300 years ago. The adhesive bonding of thin layers of a material to build up a laminate was used with various types of wood (plywood) for thousands of years. The earliest known occurrence of plywood was in ancient Egypt around 3500 B.C. when wooden articles were made from sawed veneers glued together cross-wise. This was originally done due to a shortage of fine wood. Thin sheets of high-quality wood were glued over a substrate of lower quality wood for cosmetic effect, with incidental structural benefits. This manner of inventing plywood has occurred repeatedly throughout history.

In early aircraft, adhesive bonding was used to build up wood structures for frames, contoured ribs, and spars. Wooden parts were generally laminated with various fiber directions to create sufficient strength. By laminating wood, the best properties were obtained by using the highest quality materials available and improved the stability of structures. The irregularities of grain often resulted in uncontrollable warping and cracking if any attempt is made to use the wood in thicknesses much greater than the typical veneer thicknesses (1–2 mm). High-strength plywood was used for aircraft skin molding in the 1930s and 1940s and made from birch. By combining laminated wood fiber orientations, properties could be tailored as in advanced composites and hybrid laminates today.

Protein-based adhesives (hide glues) were used in the early days with the disadvantage that these structures were sensitive to moisture. This problem was solved with the introduction of the synthetic polymers (i.e., urea-formaldehyde and phenol-formaldehyde-based adhesive systems. With the development of synthetic polymeric materials, higher loaded joints in more demanding applications became possible.

Around 1938, Aero Research Ltd. (Duxford, England) started investigating metal bonding that led to the introduction of the Redux adhesive system. This system, based on phenol-formaldehyde resin toughened with polyvinylformaldehyde thermoplastic particles and is still available in the market today.

The adhesive, Redux 775, was used by DeHavilland in the first application of metal adhesive bonding in the Hornet fighter aircraft, a derivative of the famous Mosquito aircraft. The aircraft first flew in 1944 and had a mixed wood/aluminum structure. The wing had a lower skin, leading and trailing edge, and spar caps on aluminum alloy. To ease the manufacturing, a layer of veneer was bonded to the aluminum parts (high pressure and temperature) and as an assembly step, the wood-on-wood joint was bonded with urea formaldehyde (Aerolite) adhesive cured at room temperature.

The first large-scale application of structural adhesive bonding was in the fuselage (stiffened panels) of the first jet airliner, the De Havilland Comet. Along in this time period, adhesive bonding came into its own with the first of many in a family of all-aluminum sheet metal and the honeycomb-guided missile, Matador, followed by Mace, Bullpup, Lacrosse, Pershing, Sargent, Sprint, and others. Since these early applications, adhesive bonding technology has developed much further over the years. This has led to many examples ranging from adhesive-bonded doublers on fuselage skins to large fully integrated built-up wings and fuselage structures in which stringers, doublers, and skin are cured in one single cycle. More on these examples under the applications section.

Basics

In order to produce successful bonds it is critical, in addition to surface treatment, to do the following:

1. Thoroughly mix and precisely proportion resin and hardener before application.
2. Curing temperature and times must be correct.
3. Jigs and other fixtures should securely hold bonded surfaces during curing and eliminate any movement before the part attains handling strength.
4. Bonded surfaces need only light pressure during assembly as the adhesive cures, but pressure should be applied as evenly as possible over the entire bond area. Excessive pressure can force adhesive to run out, leaving a joint starved of adhesive. Under lab conditions, pressure applied is generally 30–50 N for a bonding area 312.5 mm^2 (0.625 in^2). This figure may change for high-viscosity adhesives.
5. Durable joints must be designed properly and engineers must evaluate all the forces that will act on the bond line such as shear, tension, or compression. Butt joints and bond lines that will see peel and/or cleavage forces should be avoided. In addition, a glue line of 0.05–0.2

mm (0.002–0.008 in.) is best for optimum adhesive strength, although many thixotropic/paste adhesives can fill some of the gap between two substrates.

- 6. Adhesive selection depends on operating conditions. An assembly subjected to vibration or impact, for example, should use a toughened adhesive. Adhesive choice should also account for service conditions. Loading, temperature, and other environmental factors can all have major effects on bond strength.

Comparison of Joints

In contrast to other joining methods, such as riveting and bolting, adhesive bonding has no adverse effect on the material characteristics of the surfaces to be joined, for example, drilling of holes damaging the joined parts and creating stress concentrations (Figure 2.1). Due to this, bonded joints will have good fatigue properties. There is also no adverse effect on mechanical properties of high temperatures or distortion by local heating, as is the case with most welding or soldering processes.

In the manufacturing environment, bonding technology makes sure that the characteristic material properties are utilized to the utmost. For example, sandwich structures, in which high-strength materials are used as face sheets with a relative weak material, such as foam that is used as a core, show an excellent bending stiffness over weight ratio. Furthermore, adhesive-bonded joints create the possibility for new structural design solutions. By laminating, materials can be created with improved, often tailored characteristics compared to the properties of individual layers.

Next to the advantages mentioned, some disadvantages have to be considered. Adhesive-bonded joints are difficult to disassemble. If, for any reason, disassembly of components is desirable during the lifetime of a product then mechanically fastened joints are the preferred option. As the adhesive materials are often weaker than the substrate materials, adhesive-bonded joints

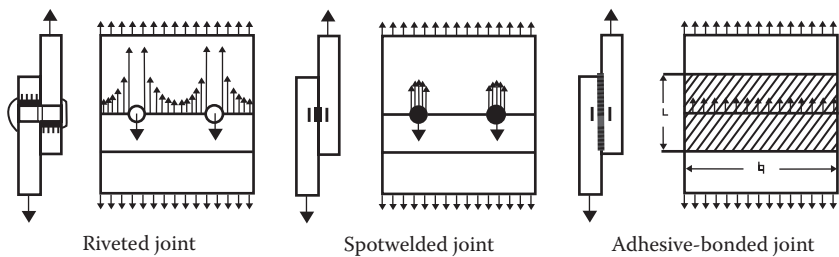


FIGURE 2.1
Comparison of stress distributions of various types of joints.

have to be designed mainly as shear loaded joints (like in riveted joints). This requires different design solutions than for bolted or welded joints.

Preparation of Surfaces for Adhesive Bonding

All substrates should be degreased and, typically, lightly abraded before bonding. But the way to get the maximum strength and long-term resistance to deterioration is through a chemical or electrolytic pretreatment, particularly on thermoset and thermoplastic surfaces. Bonds are stronger with properly prepared surfaces. Pretreatment removes low-surface energy contaminants such as waxes, oils, greases, plasticizers, and release agents. Proper preparation also reduces dust, dirt, and loose particles resulting from abrasion. Substrate pretreatment expands the surface area available for bonding by creating textured surfaces. In addition, surface preparation promotes the thorough adhesive wetting needed for strong bonds. It does so by giving the bonded material higher surface energy than that of the adhesive.

Metal substrates exhibit much higher surface energies than polymers. As a result, they are easier to wet-out and bond with adhesive-like epoxies that have surface energies around 40 mJ/m². Conversely, polymers don't wet-out as well because their surface energies are slightly lower than those of epoxy adhesives. That's why their surface energy must be raised to get a strong bond. A variety of techniques can accomplish this. These methods also help produce joints that better withstand moisture and aggressive chemicals without disbonding. In most cases, abrading surfaces and wiping them with a solvent such as acetone, ethanol, or isopropanol will be enough. But certain plastics may need flame, corona, or other chemical pretreatments to change their surface textures.

Surface Preparation for Various Materials

A key element in achieving maximum joint strength is good preparation of the substrate surface of a material. Designers must include this preparation process when selecting the substrate and adhesive that provide desired joint properties. Poor surface preparation often results in reduced joint strength. This region on the bond depends on the substrate's chemical composition and processing methods that may produce undesirable surface conditions. For example, metal oxides often form on metallic substrates during processing or storage. Plastics can have impurities on their surface related to processing or as a result of the bonding process.

The mechanical and physical properties imposed by the application often dictate the substrate composition. But all metal, plastic, elastomer, and ceramic substrates require cleaning or surface modification. This preparation boosts the surface energy that promotes wetting of the adhesive and subsequent adhesion. A surface that produces the best bond is clean and free of contamination, uniform and continuous in finish, and stable with high-surface energy. See Tables 2.1 through 2.4.

TABLE 2.1
Adhesive Selection

	Acrylic	Anaerobic	Cyanoacrylate	Epoxy	Hot Melt	Polyurethane	Polysulfide	Silicone	Solvent Base	Water Base	UV
Viscosity	Medium	Low	Low	Medium to thick	Thick	Medium	Thick	Thick	Low to medium	Low to medium	Low to medium
Void filling	Good	Poor to fair	Poor to fair	Very good	Very good	Good	Very good	Very good	Fair	Poor	Low to medium
Heat resistance	Good	Good	Fair	Good	Poor to fair	Fair	Good	Very good	Good	Fair	Fair
Cold resistance	Good	Good	Fair	Fair	Fair	Good	Good	Very good	Good	Fair	Good
Flexibility	Good	Good	Poor to fair	Fair	Fair to good	Good	Good	Very good	Good	Poor	Good
Chemical resistance	Good	Good	Good	Good	Fair	Good	Very good	Very good	Good	Poor	Fair
Humidity resistance	Good	Good	Fair	Good	Good	Fair	Good	Very good	Good	Poor	Good
Work time	Medium to fast	Medium	Fast	Slow to medium	Fast	Slow to medium	Medium	Slow to medium	Slow to medium	Medium	Slow
Cure time	Medium to fast	Medium	Fast	Slow	Fast	Medium	Medium	Medium	Medium	Medium	Fast
Metal bond (steel, aluminum)	Good	Fair	Good	Good	Fair	Good	Good	Fair	Good	Poor	Good
Plastic bonding (ABS, styrene)	Very good	Poor	Very good	Fair	Fair	Very good	Fair	Fair	Fair	Poor	Good
Polylefin	Fair	Not suggested	Good	Poor	Poor	Good	Not suggested	Fair	Fair	Poor	Fair
Wood	Not suggested	Not suggested	Not suggested	Good	Very good	Not suggested	Not suggested	Not suggested	Good	Very good	Fair
Paper	Not suggested	Not suggested	Not suggested	Not suggested	Very good	Not suggested	Not suggested	Not suggested	Good	Very good	Fair
cardboard											

Source: Ellsworth Adhesives, Germantown, Wisconsin

TABLE 2.2

Surface Pretreatments of Common Metals and Ceramics

Substrate	Solvent Cleaning ^a	Intermediate Cleaning	Chemical Treatment or Other
Aluminum	Chlorinated solvent, ketone, or mineral spirits ^b	Detergent scrub	Sulfuric (96%) acid/sodium dichromate (77.8/22.2 pbw) solution at 25°C for 20 min; rinse with tap water followed by distilled water, dry for 30 min at 70°C
Beryllium/copper	Chlorinated solvent, ketone, or mineral spirits ^b	Wet abrasive blast	—
Copper	Chlorinated solvent, ketone, or mineral spirits ^b	Dry abrasion or wire brushing	Nitric (69%) acid/ferric chloride/distilled water (12.4/6.2/81.4 pbw) solution at 21–32°C for 1–2 min; rinse in tap water followed by distilled water; dry at 65°C maximum
Steel (stainless)	Chlorinated or aromatic solvent ^b	Heavy-duty alkaline cleaner	Nitric (69%) acid/distilled water (20/80 pbw) solution at 21–32°C for 25–35 min; rinse with tap water followed by distilled water; dry at 65°C maximum
Steel (mild)	Same as stainless	Same as stainless	Ethyl alcohol (denatured)/orthophosphoric (85%) acid (66.7/33.3 pbw) solution at 60°C for 10 min; rinse in tap water followed by distilled water; dry for 60 min at 120°C
Titanium, titanium alloys	Ketone or aromatic solvent	Mild alkaline cleaner or wet abrasive scour	Nitric (69%) acid/hydrofluoric (60%) acid/distilled-water (28.8/3.4/67.8 pbw) solution at 38–52°C for 10 to 15 min; rinse with tap water followed by distilled water; dry 15 min at 71–82°C; brush off carbon residue with nylon brush while rinsing
Ceramic	Ketone solvent	—	Sulfuric (96%) acid/sodium dichromate/distilled water (96.6/1.7/1.7 pbw) at 20°C for 15 min; rinse with tap water followed by distilled water; dry at 65°C maximum

Source: Ellsworth Adhesives, Germantown, Wisconsin

^a Immerse, spray, or wipe.^b Or vapor degrease with chlorinated solvents.

TABLE 2.3
Surface Pretreatments of Common Plastics

Substrate	Solvent Cleaning ^a	Intermediate Cleaning	Chemical Treatment or Other
Acetal (Delrin)	Ketone solvent	Dry abrasion or wet or dry abrasive blast	Sulfuric (96%) acid/potassium dichromate/distilled water (88.5/4.4/7.1 pbw) solution at 25°C for 10 sec; rinse with tap water followed by distilled water and dry at room temperature
ABS	Ketone solvent	Dry abrasion or wet or dry abrasive blast	Sulfuric (96%) acid/potassium chromate/distilled water (65/7.5/27.5 pbw) solution at 60°C for 20 min; rinse with tap water followed by distilled water; dry with warm air
Polycarbonate (PC)	Alcohol	Dry abrasion or wet or dry abrasive blast	—
Polyethylene (PE) and polypropylene (PP)	Ketone solvent	—	Sulfuric (96%) acid/sodium dichromate/distilled water (88.5/4.4/7.1 pbw) at 70°C for 60 sec; expose surface to gas burner flame until the substrate is glossy. Can also be treated with corona discharge or flame.

Source: Ellsworth Adhesives, Germantown, Wisconsin

^aImmerse, spray, or wipe.

Surface energy defines the ability of adhesives and pressure-sensitive adhesive tapes to wet-out on to the substrate surfaces and promote adhesion. Materials with a low surface energy—including olefin-based thermoplastics and polypropylene—may need priming or flame or corona treating before they can take an adhesive. These pretreatments convert low surface energy substrates to a higher surface energy better suited for strong adhesive bonds. Likewise, anodizing aluminum surfaces is one method that will boost reliability of adhesive-bonded joints incorporating those materials. Anodizing increases surface roughness, resulting in a significant improvement in mechanical adhesion behavior of the substrate.

Solvent Wipe

This is the simplest form of surface preparation and is ideal for removing waxes, oils, and other low-molecular weight contaminants from substrates. The technique relies on the contaminants being soluble in the solvent and the solvent itself being free of dissolved contaminants. But some solvents aren't

TABLE 2.4

Prepped to Bond

Substrate	Recommended Pretreatments
Aluminum	Solvent degrease and 20–40 min etch in 140–150°F sulfuric acid and sodium dichromate or ceramic grit blast
Copper, brass, and their alloys	Ferric chloride/nitric acid etch or ammonium sulfate/water etch
Steels (nonstainless)	Solvent degrease and etch in diluted sulfuric or hydrochloric acid
Stainless	Solvent degrease, etch in concentrated sulfuric acid 20–30 min
Nickel and its alloys	Abrasive or solvent clean, etch in sulfuric acid or sulfuric/nitric acid pickle
Titanium	Abrasive or solvent clean, acid etch at room temperature
Zinc	Abrade then degrease or vapor clean, or acid etching
Silica ceramics and glasses	Abrade, apply silicone primers, solvent clean
Silicon carbide	Abrade, solvent clean
Carbons and carbon fibers, zirconia ceramics	Abrade, solvent clean, apply primers
Epoxies, phenolics, and polyesters	Abrade, solvent clean, apply primers
Polyimides and polyether ketones	Abrade, solvent clean, and degrease
Fluoropolymers (Teflon, PTFE, etc.), silicones	Apply special primers

Note: Surface preparation is the key to an adhesive bond that will last, even at high temperatures. These are the recommended treatments for some common substrates.

compatible with particular polymeric substrates. Some solvents dissolve thermoplastics or will create stress cracking or crazing on surfaces. Common solvents are acetone, MEK (methyl ethyl ketone), MIBK (methyl isobutyl ketone), xylene, TCE (trichloroethylene), ethanol, and IPA (isopropyl alcohol).

Solvents should be applied with clean, lint-free cloths, or paper towels. Take care to prevent cross-contamination from sample to sample by not reusing cloths or dipping a contaminated cloth dipped into the solvent. It's also important to monitor for hazardous and toxic-vapor buildup when using solvents. Solvent wiping is not suitable for large-scale bonding projects. Instead, vapor degreasing or ultrasonic vapor degreasing are more appropriate.

Abrasion

This can be accomplished several ways. Manual abrasion includes wire brushing, paper sanding, and filing. Automated techniques include high speed sanding, grinding, and shot/grit blasting. Mechanical/automated abrasion processes are relatively quick and economical. They are also reproducible and depend less on skilled labor than manual methods.

Flame Treatment

This technique partially oxidizes surfaces, producing polar groups that raise the polymer's surface energy. This technique uses a gas or gas/oxygen flame. It works well for uneven profiles and thick substrates. It is easy to adjust and control the gas/oxygen ratio, flow rate, exposure time, and proximity of flame to the substrate. It is an effective method for use on PE (polyethylene) and PP (polypropylene). Thinner substrates are better suited to corona pretreatment.

Plasma Treatment

The process uses a plasma created by charging a gas with a high amount of energy. The free ions and electrons in the plasma clean the surfaces of any material it touches. On organic surfaces, plasmas, like flames, create polar groups/active radicals that boost surface energy and aid adhesion. Low pressure plasma is a technique that involves exciting a gas with high frequency and high voltage between two electrodes in a low pressure chamber. The process uses various plasmas of argon, ammonia, nitrogen, or oxygen, which make it suitable for a wide range of substrates.

With low pressure plasmas, air can serve as the plasma source. In this case, oxygen in air produces the greatest results because it reacts with carbohydrate-based contaminants and breaks up large-chain molecules. Handheld and automated devices are available for the method. Some devices can be fit to a robotic head so adhesives can go on immediately after pretreatment. The process creates surfaces with energies greater than 70 mJ/m² in many cases.

Low pressure plasma has an active bandwidth of 1.27 cm (0.5 in.). It can be used at up to 3000 fpm and its a candidate for large industrial applications. Among the plastics suitable for treatment with low pressure plasma are PP, PE, polyamide, polyethylene terephthalate (PET), acrylonitrile butadiene styrene (ABS), polycarbonate (PC), rubber, and composites.

Corona Discharge

This effect works like low pressure plasma in principle, but events take place in the air at atmospheric pressure. A corona is generated by applying high voltage (up to 30 kV) at frequencies ranging from 9 to 50 kHz to an electrode separated from a grounded table by an air gap. At 3–5 kV/mm, a current passes through the air gap to generate free electrons that move toward the positive electrode with great energy. The free electrons displace electrons from molecules in the air gap and, in turn, create more free electrons. The corresponding ions contribute to a current that flows across the gap. As ionization currents rise, the corona discharge rate also increases (i.e., the particles move faster). The resulting plasma then activates the surface of the

plastic part onto which the discharge is directed. Corona discharge is especially well suited for thin films and composite laminates.

Chemical Treatment

It works well for bonding polymeric substrates. These treatments are usually applied by polymer manufacturers or companies specializing in chemical treating. Treatments used for polymers include etchants for polytetrafluoroethylene (PTFE), caustic soda etching for polyesters, proprietary primers for PP, sulfuric acid for polysulfide (PS), and the Sicor process for thermoplastics. Sicor was developed by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Australia, primarily for the automotive industry.

Laser

Recently demonstrated was the use of a low power handheld laser system that could be used to pretreat aircraft surfaces prior to adhesive bonding surface preparation via a sol-gel process that uses a specific chemistry. Engineers conducted tests with a prototype laser system to validate this promising method for removing organic coatings, contaminants, and an oxide layer from aluminum surfaces in an environmentally friendly manner. Scientists also studied the surface morphology and chemistry produced by the laser pretreatment to determine how bond strength and moisture durability correlate with surface characteristics, and to compare laser pretreatment with other pretreatment methods.

Chemical paint stripping methods and sandblasting techniques create large amounts of waste and residue that require careful handling and disposal. Due to increasing restrictions and safety concerns raised by government agencies and commercial industry regarding these processes, material scientists have identified laser technology as a potential, environmentally friendly alternative. Engineers demonstrated that the use of a handheld laser can also eliminate laborious and time-consuming surface pretreatment processes required for conventional aircraft metal bonding techniques. A prototype handheld laser end effector using a commercially available, 10 W, neodymium (Nd): yttrium aluminum garnet (YAG) laser system was previously researched by laboratory engineers who were investigating laser cleaning of aircraft oxygen tubes and recognized the laser technology's potential for environmentally friendly surface cleaning and paint stripping.

During an initial laser surface pretreatment for metal adhesive bonding project, engineers optimized and evaluated the system's ability to remove organic coatings and to clean, deoxidize, and texturize the surface for bonding. They demonstrated the technology as an environmentally favorable alternative to chemically stripping, hand sanding, grit blasting, and chemically cleaning metallic surfaces. They also proved through lap shear, 90°, peel, and wedge crack extension testing that acceptable bond strength and

moisture durability are attainable on a surface contaminated by baked-on hydraulic fluid prior to laser pretreatment and sol-gel surface preparation.

The Air Force Research Laboratory initiated a follow-up project to determine if commercial, handheld laser systems can properly strip, clean, deoxidize, and provide the surface morphology required for acceptable adhesively bonded aircraft repairs. Once again, engineers utilized the water-based, nonchromated sol-gel technology as the bonding treatment. In the final phase of the project, engineers plan to evaluate the Nd:YAG laser's capability to prepare titanium (using sol-gel) and composite surfaces for adhesive bonding.

Joint Design and Proper Adhesive Selection

The two most important considerations needed to achieve the following properties are careful joint design and proper adhesive selection.

- Uniform stress distribution and larger stress-bearing area.
- Outstanding fatigue as well as mechanical and thermal shock resistance.
- Continuous contact between substrates, producing good seals, and load-bearing properties.
- Can bond dissimilar substrate materials including metals, plastics, elastomers, ceramics, glass, and wood.
- Can bond different substrates at low or elevated temperatures.
- Smooth, contour-free surfaces, free from external projection and gaps.
- Less critical tolerances when components are joined because of gap-filling capability.
- Minimized galvanic (electromechanical) corrosion between dissimilar metal substrates.
- Thermal and/or electrical insulation or conductivity.
- Wide service temperature range capability.
- Long-term durability.
- Resistance to thermal or mechanical shock and vibrations.

Joint design requires the selection of an appropriate style, proper surface preparation, and use of careful application and assembly procedures. Special attention must also be given to the following recommended adhesive curing procedures. Joint design should minimize stress concentrations so the load is distributed over the entire area.

Joint design should be selected to enhance bond strength for the specific use under consideration. Popular joints used in structural bonding applications

include butt, scarf, lap, and offset lap. Butt joints are used when stress concentrations are concentrated along the bond line and when forces perpendicular to the bond are minimal. Scarf joints allow for an ample adhesive bond area, but parts joined in this way must maintain closer fits. Lap and lap offset joints are recommended for thin sections and rigid parts. In lap joints, the bonded parts are slightly offset, thus peel and cleavage forces develop when the joints are under load. These forces can be minimized by using the offset lap joint design.

Surface preparation is critical for achieving high-strength structural bonds. Surfaces contaminated with oils, greases, dirt, moisture, and other contaminants must be carefully cleaned prior to adhesive application. Certain forms of oxidation, notably loose rust, must be completely removed. Other metallic substrates are preferred. The adhesive supplier's recommendation should be carefully followed to assure good results. Curing conditions must be duplicated to achieve desired performance.

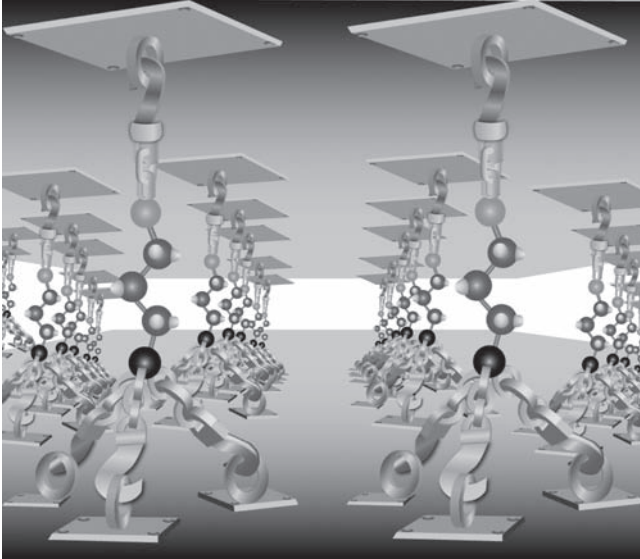
Adhesive Types

The choice of adhesive makes a difference thus it is critical to produce durable joints.

Nanoglue

An adhesive based on self-assembling nanoscale chains for bonding materials that do not normally stick together is under development at Rensselaer Polytechnic Institute, Troy, New York. The glue material is already commercially available, but the research team's method of treating the glue to dramatically enhance its "stickiness" and heat resistance is completely new. The nanoglue nanolayer is sandwiched between a thin film of copper and silica, which strengthens the bond and boosts adhesive properties. Less than a nanometer thick, the nanoglue is inexpensive to make and can reportedly withstand temperatures far higher than what was previously envisioned. See Figure 2.2. When exposed to heat, the middle layer of the "nanosandwich" does not break down or fall off, as it has nowhere to go. Constrained between the copper and silica, the nanolayer's molecules hook onto an adjoining surface with unexpectedly strong chemical bonds. In addition, the nanolayer's bonds grow stronger and more adhesive when exposed to temperatures above 400°C (750°F) [2].

In another study iron oxide nanoparticles were inbedded in nanoparticles of silicon dioxide in a variety of adhesives that enables both bonding and disbonding by application of high-frequency alternating magnetic fields. The adhesives contain the MagSilica filler, which is nanostructured and contains a powder of superparamagnetic particles. When the adhesives are exposed to a high-frequency alternating magnetic field, the particles oscillate and heat the adhesive. This causes one- and two-component adhesives to harden

**FIGURE 2.2**

Self-assembling nanoglue can bond nearly anything together.

within seconds. The bonds can be dissolved by exposing the adhesive bond to another high-frequency magnetic field. This field has the same frequency as during hardening, but a higher intensity. For the method to work, at least one of the components to be bonded must be electrically nonconducting.

Flexible

Flexible adhesives provide joints with a more uniform distribution and less of a difference between average and maximum stress. These adhesives distribute peel and shear stresses over a larger area thereby improving joint efficiency. However, since adhesives with high flexibility and elongation typically have lower cohesive strength than more rigid adhesives, the advantage of flexibility and high elongation is usually compromised. In order to transfer the same load a much larger overlap is needed.

Three structural adhesives have been designed to produce strong, flexible bonds on composites and offer medium to long working times for large assemblies. The products are said to be ideal for use on boats, trucks, buses, architectural ornamentation, wind turbine blades, and composite bridges and decks. MA530, MA560-1, and MA-590 are two-part methacrylates that can be dispensed manually or with standard meter-mix equipment. The 100% reactive, nonsagging gels have been recommended for joining composite assemblies, ABS, acrylics, gel-coats, polyesters including DCPD modified (dicyclopentadiene), polyvinyl chloride (PVC), styrenics, and vinyl esters. They require little or no surface preparation and cure at

room temperature to produce bonds that withstand service temperatures of -40 – 82°C (-40°F – 180°F).

MA530 has a working time of 30–40 minutes and fills gaps up to 17.78 mm (0.70 in.). A 0.76 mm (0.03 in.) bond line achieves approximately 75% of its ultimate shear strength in 90–160 minutes at 23.3°C (74°F), according to preliminary tests. MA560-1 has a longer working time (55–70 minutes) and fills gaps up to 2.54 cm (1 in.). It is recommended for large structures as well as small part assembly where fewer workers are required. Fixture time for a 0.76 mm (0.03 in.) bond line is 220–240 minutes at 23.3°C (74°F). MA590 has a long working time of 90–105 minutes and was formulated for building large fiber reinforced plastics (FRP) boats. A 0.76 mm (0.03 in.) bond line achieves approximately 75% of its ultimate shear strength in 180–240 minutes at 23.3°C (74°F). This adhesive fills gaps up to 2.54 cm (1 in.).

For flexible joints, the latest polyurethanes and modified silanes withstand vibration and provide long-term durability. They are used for window glazing and roof-panel bonding on heavy-duty construction equipment, trailers, utility trucks, agricultural equipment, and school buses.

Pressure-Sensitive

A manufacturer of pressure-sensitive adhesives, says patient comfort can be a difficult goal when it comes to adhesives used on bandages for covering wounds or holding catheters in place. Sometimes medical devices must stick to skin for long periods of time while withstanding showering and exercising. New silk adhesives have been developed with good skin adhesion that can be removed cleanly and gently without hurting the skin. In addition, the adhesives are okay for sustained skin contact and remain suitable after sterilization. These new silk adhesive systems allow engineers to select adhesives with strength, quick tack, peel strength from skin, shear strength, and removability.

Waterproof Bandages

A newly developed waterproof adhesive bandage inspired by Gecko lizards may soon join sutures and staples as a basic operating room tool for patching up surgical wounds or internal injuries reported by MIT researchers. The MIT researchers built the adhesive with a biorubber and, using micropatterning technology, shaped the biorubber into different hill and valley profiles at nanoscale dimensions.

The surface of the bandage has the same kind of nanoscale hills and valleys that allow the lizards to cling to walls and ceilings. Applied over this landscape is a thin coating of sugar-based glue that helps the biodegradable bandage stick in wet environments, such as to heart, bladder, or lung tissue. Because it can be folded or unfolded, the bandage is potentially suitable for minimally invasive surgical procedures that are performed through a very

small incision. The adhesive could also be infused with drugs designed to release as the biorubber degrades. The elasticity and degradation rate of the biorubber are tunable as is the pillared landscape—allowing for customizable elasticity, resilience, and grip for different medical applications [3].

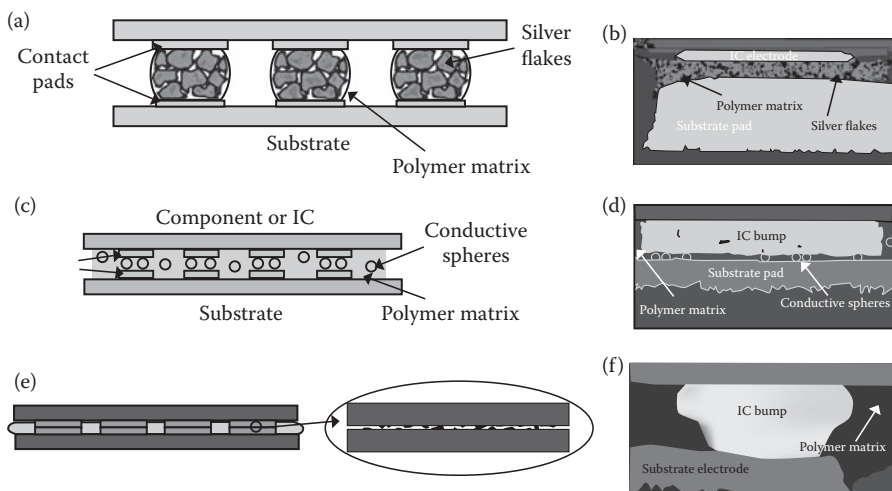
Electrically Conductive Adhesives

Electrically conductive adhesives (ECAs) are composites of polymeric matrices and electrically conductive fillers. The polymeric resin, such as an epoxy, silicone, or polyimide, provides physical and mechanical properties such as adhesion, mechanical strength, impact strength, and the metal filler (such as silver, gold, nickel, or copper) conducts electricity. Recently, ECA materials have been identified as one of the major alternatives for lead-containing solders for microelectronics packaging applications. ECAs offer numerous advantages over conventional solder technology, such as environmental friendliness, and mild processing conditions (enabling the miniaturization of electronic devices) [4–7]. Therefore, conductive adhesives have been used in flat panel displays such as liquid crystal display (LCD), and smart card applications as an interconnect material and in flip-chip assembly, chip scale package (CSP) and ball grid array (BGA) applications in the replacement of solder. However, no currently commercialized ECAs can replace tin-lead metal solders in all applications due to some challenging issues such as lower electrical conductivity, conductivity fatigue (decreased conductivity at elevated temperature and humidity aging or normal use condition) in reliability testing, limited current-carrying capability, and poor impact strength. Table 2.5 gives a general comparison between tin–lead solder and generic commercialized ECAs [8,9].

Depending on the conductive filler loading level, ECAs are divided into isotropically conductive adhesives (ICAs), anisotropically conductive adhesives (ACAs), and nonconductive adhesives (NCAs). For ICAs, the electrical conductivity in all *x*-, *y*-, and *z*-directions is provided due to high filler content exceeding the percolation threshold. For ACAs or NCAs, the electrical

TABLE 2.5
Conductive Adhesives Compared With Solder

Characteristic	Sn/Pb Solder	ECA
Volume resistivity	0.000015 Ohm-cm	0.00035 Ohm-cm
Typical Junction R	10–15 mW	<25 mW
Thermal conductivity	30 W/m ² K	3.5 W/m ² K
Shear strength	2200 psi	2000 psi
Finest pitch	300 μm	<150–200 μm
Minimum processing temperature	215°C	150–170°C
Environmental impact	negative	very minor
Thermal fatigue	yes	minimal

**FIGURE 2.3**

Schematic illustrations and cross-sectional views of (a,b) ICA, (c,d) ACA, and (e,f) NCA flip chip bondings.

conductivity is provided only in the z -direction between the electrodes of the assembly. Figure 2.3 shows the schematics of the interconnect structures and typical cross-sectional images of flip-chip joints by ICA, ACA, and NCA materials illustrating the bonding mechanism for all three adhesives.

Isotropically Conductive Adhesives (ICAs)

Isotropic conductive adhesives, also called polymer solder, are composites of polymer resin and conductive fillers. The adhesive matrix is used to form a mechanical bond for the interconnects. Both thermosetting and thermoplastic materials are used as the polymer matrix. Epoxy, cyanate ester, silicone, polyurethane, and so on are widely used thermosets; and phenolic epoxy, maleimide, acrylic, preimidized polyimide, and so on are the commonly used thermoplastics. An attractive advantage of thermoplastic ICAs is that they are reworkable (i.e., can easily be repaired). A major drawback of thermoplastic ICAs, however, is the degradation of adhesion at high temperatures. Another drawback of polyimide-based ICAs is that they generally contain solvents. During heating, voids are formed when the solvent evaporates. Most commercial ICAs are based on thermosetting resins. Thermoset epoxies are by far the most common binders due to the superior balanced properties, such as excellent adhesive strength, good chemical and corrosion resistances, and low cost, while thermoplastics are usually added to allow softening and rework under moderate heat. The conductive fillers provide the composite with electrical conductivity through contact between the conductive particles. The possible conductive fillers include silver, gold, nickel,

copper, and carbon in various forms (graphites, carbon nanotubes, etc.), sizes, and shapes. Among different metal particles, silver flakes are the most commonly used conductive fillers for current commercial ICAs because of the high conductivity, simple process, and the maximum contact with flakes. In addition, silver is unique among all the cost-effective metals by nature of its conductive oxide.

Oxides of most common metals are good electrical insulators, and copper powder, for example, becomes a poor conductor after aging. Nickel and copper-based conductive adhesives generally do not have good resistance stability, because both nickel and copper are easily oxidized. ICAs have been used for die attach adhesives. Recently, ICAs have also been considered as an alternative to tin/lead solders in surface mount technology (SMT), flip-chip, and other applications and a large amount of effort and development has been conducted to improve the properties of ICAs in the past years [10–14]. An ICA is generally composed of a polymeric binder and silver flakes. There is a thin layer of organic lubricant on the silver flake surface. This lubricant layer plays an important role for the performance of ICAs, including the dispersion of the silver flakes in the adhesives and the rheology of the adhesive formulations [15,16].

Anisotropic Conductive Adhesives (ACAs/ACFs)

Anisotropic conductive adhesives (ACAs) or anisotropic conductive films (ACFs) provide unidirectional electrical conductivity in the vertical or Z-axis. This directional conductivity is achieved by using a relatively low volume loading of conductive fillers (5–20 vol.%). The Z-axis adhesive, in film or paste form, is interposed between the surfaces to be connected. Heat and pressure are simultaneously applied to this stack-up until the particles bridge the two connector surfaces.

The ACF bonding method is a thermocompression bonding process shown in Figure 2.4. Interconnection technologies using ACFs are major

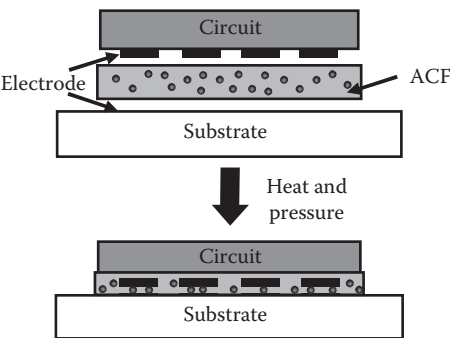


FIGURE 2.4
Thermocompression bonding using ACF.

packaging methods for flat panel display modules and have high resolution, light weight, thin profile, and low consumption power. In addition to the LCD industry, ACA/ACF is now finding applications in flex circuits and SMT for chip-scale package (CSP), application specific integrated circuit (ASIC), and flip-chip attachment for cell phones, radios, personal digital assistants (PDAs), sensor chip in digital cameras, and memory chip in laptop computers. The ACA/ACF joints generally have lower electrical conductivity, poor current carrying capability, and electrical failure during thermal cycling.

Nonconductive Adhesive/Films (NCAs/NCFs)

Electrically conductive adhesive joints can be formed without any conductive fillers. The electrical connection of NCAs is achieved by sealing the two contact partners under pressure and heat. Thus, the small gap contact is created, approaching the two surfaces to the distance of the surface asperities, as illustrated in Figure 2.3e. The formation of contact spots depends on the surface roughness of the contact partners. Approaching the two surfaces enables a small number of contact spots to form that allows the electric current to flow. When the parts are pressed together during the sealing process, the number and area of the single contact spots are increased according to the macroscopic elasticity or flexibility of the parts and the microhardness and plasticity of the surfaces, respectively.

Conductive joints with NCA/NCF provide a number of advantages compared to other adhesive bonding techniques. NCA/NCF joints avoid short-circuiting and are not limited, in terms of particle size or percolation phenomena, to a reduction of connector pitches. The size reduction of electronic devices can be realized by the shrinkage of the package and the chip. Further advantages include cost-effectiveness, ease of processing regarding the possibility of nonstructures adhesive application, good compatibility with a wide range of contact materials, and low temperature cure. In fact, the pitch size of the NCF joints can be limited only by the pitch pattern of the bond pad, rather than the adhesive materials.

Summary

Polymer metal-based, electrically conductive adhesive has been evolved to meet the high electrical/mechanical/thermal performance, fine pitch capability, low temperature process, and strong adhesion/reliability requirements for electronic packaging module and assemblies. As one of the most promising, lead-free alternatives in electronic and optoelectronic device packaging interconnect materials, electrically conductive adhesives have shown remarkable advantages and attracted many research interests. Significant improvements in the electrical, mechanical, thermal properties of different types of conductive adhesives have been achieved. Electrically conductive

adhesives with high performance and acceptable reliability have been developed for applications in die attach, flip-chip, and surface-mount interconnect applications. These lead-free materials and processing methods have great potential to replace the lead-containing solders in the electronics industry.

Conductive

A new conductive adhesive technology has recently been introduced to the marketplace, delivering dramatic improvements in thermal performance, drop test reliability, and providing significant personnel and equipment savings. With this new technology, the traditional mixing and measuring of previous systems (not to mention the issues associated with managing pot life) are completely eliminated. The advanced adhesive technology, called Bead-On-Bead, is a remarkable new product that has the potential to completely change the way the market thinks about adhesive systems.

Loctite Bead-On-Bead technology is a two-part system based on proprietary technology that enables simple, yet incredibly strong, bonding of heat-dissipating devices to heat sinks and spreaders. Ease of use is one of the premiere benefits of this extraordinary system. Bead-On-Bead requires no meter mixing, no volumetric measuring, no management of pot life and, because of its color characteristics, visual inspection is made easy. Each part (parts A and B) are applied to the electronic device and heat dissipating device separately, so no mixing is required. When parts A and B combine during assembly, cure is achieved and fixture strength is realized within seconds. All of these process enhancements come with the added benefit of improved thermal performance. The product has a thermal conductivity of $1.75\text{W/m}^\circ\text{K}$, which is a 40% improvement over the older generation products.

The Bead-On-Bead adhesive technology has been applied to an light emitting diode (LED) and a heat sink in a flashlight and by adjusting the pressure for the seating of the LEDs to the heat sink combined with the robust Bead-On-Bead adhesive system, bond lines yielded joints close to 0.13 mm (0.005 in.) thick. In addition, because these flashlights are often dropped, a stringent drop test requirement was imposed of 1500 cm (50 ft), which Bead-On-Bead satisfied, delivering very high reliability.

This new technology also provided a solution for inspection. The technology provided a solution where Bead-On-Bead's unique color coded system delivered increased manufacturing control. The adhesives are colored part yellow and part blue and when the parts are assembled, the bond line becomes green, allowing for very simple visual inspection.

Another new high temperature resistance conductive glue offers an adhesive that is suitable for making an electrically conductive connection to a material or system that is operated at high temperatures or can even be a heating element. The technology was developed by Philips and SIMTech as part of the flat heating technology for clothes irons, where a need for a reliable,

strong, and cost-efficient glue was required as techniques such as soft soldering had too low a melting point and hard solder too high a melting point for use with aluminum plates. The glue developed was a super glue based on sol-gel precursors that had all the properties that were required. The product is currently commercially available in clothes irons from Philips, and is also proven in flat panel heaters where glues and adhesives were not suitable due to high temperatures and high power densities. This new adhesive utilizes complex sol-gel precursors resulting in a hybrid sol-gel material.

Structural

Recent advances in structural adhesives deliver the same strength as welds, or go through paint baking unscathed. Other new adhesives require no surface cleaning, a process that was once a given before any bonding could commence. Today's structural adhesives are formulated to withstand severe shock, peel, and impact. They bear heavy loads, withstand chemicals, endure extreme temperatures, absorb energy, and can take large deformations without rupturing.

Specialty-vehicle manufacturers, for example, now use structural adhesives to replace or augment rivets, bolts, welding, and other traditional fastening methods. Adhesives rather than fasteners assemble frames, panels, booms, and cabs. Better product aesthetics result from adhesive assembly and, thus, can greatly boost vehicle value. Structural adhesives also simplify production by eliminating the need to precisely bore holes for installation of rivets or other mechanical fasteners. Likewise, in most environments such as bathtubs and spas, structural adhesives attach and bond galvanized steel frames to fiberglass and ABS. Commercial furniture manufacturers bond plain, painted, or powder-coated metals and plastics in chairs, desks, and cabinets.

Structural-adhesive technologies include epoxies, acrylics, methylmethacrylates (MMAs), modified silanes, and polyurethanes. Adhesives can be tailored to deliver processing and performance benefits. For example, adhesives come as one-part no-mix or two-part mix systems. They can cure under ambient room temperature or at elevated temperatures in cure ovens. For high-speed assembly, there are fast-curing adhesives as well as those with long work lives for parts that need alignment once they are in place. High, medium, and low viscosity formulations can fill large gaps or provide thin, virtually invisible bond lines.

It is usual practice to add dispensing and curing equipment to a specific assembly process. This lets manufacturers optimize process efficiency, keep down waste, and make dispensing and curing repeatable and consistent. Advances in structural-adhesive technology have dramatically expanded the scope of potential bonding applications. Over time, traditional structural adhesives lose strength on substrates such as galvanized steel. Here, the zinc coatings used on the galvanized steel eventually delaminates the bond.

New structural adhesives are providing long-term durability on such hard-to-bond substrates. Prefabricated building components including galvanized trusses, joists, shear walls, headers, studs, and cantilevered beams are also adhesively bonded. Traditional structural adhesives can also have trouble maintaining long-term strength when exposed to elevated temperatures. This data is significant for a manufacturer of electric motors trying to decide whether to attach magnets using mechanical clips or adhesives. Electric motors continuously operate at elevated temperatures. Adhesive joints in the magnet assembly will gain strength over time and will withstand vibration better than mechanical fasteners.

Adhesives are also making inroads in loudspeakers that are getting smaller with each new generation. Speaker manufacturers are demanding impact and temperature-resistant structural adhesives that cure rapidly. As speakers get smaller, adhesives must also withstand high temperatures that result from tighter operating spaces. The demand for more portable speakers also means adhesives must have higher resistance to impacts. And to improve the bottom line, speaker manufacturers demand fast-fixturing adhesives to speed production, reduce work-in-process, and eliminate mechanical-fastener inventories.

Environmental considerations can also greatly affect the long-term performance of an assembly. A two-part MMA, for example, was exposed to salt, fog, and humidity for 1,000 hours. Here the adhesive maintains more than 95% of its strength when compared to the control sample, see Table 2.6. Recently introduced structural adhesives can withstand welding, phosphate pickling, and powder-coating processes while maintaining strength. And some can replace costly metallic inert gas (MIG) or tungsten inert gas (TIG) welds by bonding two substrates and supporting the bond with low-cost spot welds that hold the assembly together while the adhesive cures. These fast-fixturing, weld-tolerant adhesives let assemblies go in pickling and paint-bake processes within 20 minutes.

The MMA adhesives can bite through surface oils and contaminants, eliminating the need for surface preparation and activators. For traditional adhesives, surface preparation has always been critical to ensure a long-lasting, reliable bond. See the section earlier on surface preparation. Surface treatment requirements depend on the level of contamination, the substrates, the initial and long-term bond performance, and the financial practicality of the treatment process. For difficult-to-bond substrates such as polyolefin plastics, new adhesives bond exceptionally well within the need for primers or surface treatments.

Recently developed structural adhesives seal out moisture and gases in applications where substrates have different coefficients of thermal expansion (CTE). For example, paintable, clear, UV-resistant modified silanes are being used for bonding appliance assemblies, truck bodies, and in HVAC applications. Structural adhesive bonding offers significant technical as well as economic advantages over mechanical fasteners as well as joining

TABLE 2.6
Structural Adhesives

	Epoxy	Two-Part MMA	Two-Part Acrylic	Two-Part Urethane	Modified Silane
Benefits	High-temperature resistance, chemical resistance, low shrinkage, high shear and tensile strength, bond glass	Impact resistance; good elongation/flexibility; fills gaps; high peel, tensile, and shear strength; bonds metals, composites, and plastics	Impact resistance, high-temperature resistance, high shear and tensile strength, no mixing required, rapid cure, bonds metal and glass	High elongation/flexibility, toughness	Flexibility, paintable, sealing properties; no mixing required
Limitations	Low elongation/flexibility, low adhesion to plastics and rubbers, mixing required for two-part systems	Low adhesion to rubber, mixing required, strong odor	Need an activator, low adhesion to plastics and rubber, limited gap filling	Sensitive to moisture, mixing required, contains isocyanates	Limited temperature resistance, low resistance to nonpolar solvents, low adhesion to rubber, extended cure time

techniques such as soldering, brazing, or welding for many demanding assembly constructions. Epoxy polymer-based resin systems have become the engine for the growth of structural bonding because of their unmatched processing versatility, high-strength, low-weight, and wide-service temperature capabilities, even when exposed to hostile environmental conditions. Their strength properties can be further improved by compounding with glass, carbon, or polyimide reinforcing fibers. Both thermally conductive and also electrically conductive adhesive formulations are available and are widely used for many electrical, mechanical, and medical devices.

Fiber-reinforced, epoxy-resin composites can compete economically with steadily increasing success against conventional metal constructions both on the basis of a more favorable strength/weight ratio and enhanced corrosion-free service life. Their industrial success is demonstrated by the fact that some 60% of today's aerospace structures are manufactured with epoxy-resin adhesive systems. Other polymer adhesive candidates, such as polyimides, are mainly considered for specialty demanding applications. Thermal stability and chemical resistance as well as specific curing conditions are mainly determined by the choice of the base resin and the hardener components. The workhorse of the structural adhesives field are the so-called bisphenol A-type epoxy resins and amine type hardeners. Epoxy-base resin and hardeners can be either liquid or solid with liquids generally preferred. They are also available in the form of both supported and unsupported semi-cured films.

Depending on the choice of base resin and hardener, an epoxy-adhesive composition can cure as fast as 45 seconds or as slowly as 48 hours or more at ambient or quickly elevated temperatures. The bond strength, mechanical strength properties, toughness, flexibility, electrical and thermal conductivity, thermal and mechanical shock resistance, thermal expansion coefficients, and so on can be varied greatly depending on the selection and amount of the various other ingredients added to the base resin-hardener system. The number of such additives that can be added to optimize specific desirable processing and/or performance properties is steadily increasing. The performance of epoxy adhesives can thus be designed to maximize such characteristics as physical strength, heat stability, chemical resistance, thermal shock, and electrical insulation for different end product applications. They are used for bonding metal and nonmetallic substrates, including most plastics, ceramics, glass, and wood, as well as many elastomers.

Structural epoxy-adhesive systems feature the highest tensile strength of all commercially available bonding agents. Resistance to moisture, fuels, oils, acids, bases, and many other aggressive chemicals is of a very high order over a wide service temperature range. They can safely be operated at service temperatures from as high as 300°C (572°F) to cryogenic conditions. Most advantageous for structural design reliability are their outstanding gap-filling properties. Only positive contact pressure is generally required to effect cures at the temperature/time schedules recommended by the

adhesive manufacturer. When bonding dissimilar metals, the epoxy-adhesive bond also functions as protection against corrosion.

The most widely used epoxy adhesives are one- and two-component liquids or pastes. The two-component systems may be cured at ambient or, more quickly, at elevated temperatures. One-component formulations require a cure at elevated temperatures. Recently, one-component epoxy-types of adhesives have been introduced that can be cured in seconds by exposure to UV light. Dual cure adhesive systems capable of use by either exposure to UV light or heat have been successfully developed for certain sensitive plastic substances as well as assemblies where an ingress of UV light in selected areas is limited. Substantial technical progress has been made to enhance toughness, shear strength, thermal stability, and chemical resistance even upon prolonged exposure to hostile environments. The demands of the aerospace and defense industries for lighter-weight, high-strength, and heat-resistant structures have stimulated these developments. Manual, semiautomatic, and automatic equipment for dispensing such one- and two-component epoxy-resin adhesive composites is readily available commercially from many manufacturers.

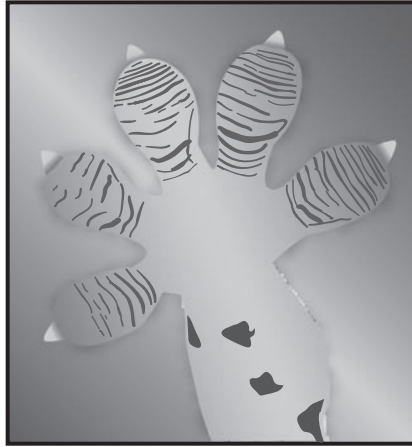
Major industrial and product applications for structural epoxies include:

- Aerospace and defense
- Oil-servicing industry
- Sporting goods
- Civil engineering structures
- Electronic assemblies
- Medical devices
- Industrial processing
- Automotive components

The number of applications are steadily growing, fueled by the increasing need for lighter weight corrosion-resistant and more cost-effective assemblies.

Animal

The race for the best “Gecko foot” dry adhesive has a new competitor with a stronger and more practical material reported in the journal *Science* [17]. Scientists have long been interested in the ability of Gecko lizards to scurry up walls and cling to ceilings by their toes. The creatures owe this amazing ability to microscopic branched elastic hairs in their toes that take advantage of atomic-scale attractive forces to grip surfaces and support surprisingly heavy loads (Figure 2.5) [17]. Several research groups have attempted to mimic those hairs with structures made of polymers or carbon nanotubes.

**FIGURE 2.5**

Closeup of a gecko foot, showing the pads that bear microscopic branched elastic hairs that use atomic-scale forces to grip surfaces.

Scientists and researchers have developed and improved carbon nanotube-based material that for the first time creates directionally varied (anisotropic) adhesive force. With a gripping ability nearly three times the previous record—and 10 times better than a real gecko at resisting perpendicular shear forces—the new carbon nanotube array could give artificial gecko feet the ability to tightly grip vertical surfaces while being easily lifted off when desired. Beyond the ability to walk on walls, the material could have many technological applications, including connecting electronic devices and substituting for conventional adhesives in the dry vacuum of space. The resistance to shear force keeps the nanotube adhesive attached strongly to the vertical surface, but you can still remove it from the surface by pulling away from the surface in a normal direction. This directional difference in the adhesion force is a significant improvement that could help make this material useful as a transient adhesive.

The key to the new material is the use of rationally designed, multiwalled carbon nanotubes formed into arrays with “curly entangled tops.” The tops (can be compared to spaghetti or a jungle of vines) mimic the hierarchical structure of real gecko feet, which include branching hairs of different diameters. When pressed onto a vertical surface, the tangled portion of the nanotubes becomes aligned in contact with the surface. That dramatically increases the amount of contact between the nanotubes and the surface, maximizing the van der Waals forces that occur at the atomic scale. When lifted off the surface in a direction parallel to the main body of the nanotubes, only the tips remain in contact, minimizing the attraction forces. In tests done on a variety of surfaces—including glass, a polymer sheet, Teflon, and even rough sandpaper—the researchers measured adhesive forces of

up to 100 Newtons per square centimeter in the shear direction. In the normal direction, the adhesive forces were 10 Newtons per square centimeter—about the same as a real Gecko lizard.

The resistance to shear increased with the length of the nanotubes, while the resistance to normal force was independent of tube length. Though the material might seem most appropriate for use by the comic book hero, Spider-Man, the real applications may be less glamorous. Because carbon nanotubes conduct heat and electrical current, the dry adhesive arrays could be used to connect electronic devices.

Thermal management is a real problem today in electronics, and if you could use a nanotube dry adhesive, you could simply apply the devices and allow van der Waals forces to hold them together and that would eliminate the heat required for soldering. Another application might be for adhesives that work long-term in space. In space, there is a vacuum and traditional kinds of adhesives dry out. But nanotube dry adhesives would not be bothered by the space environment.

For the future, researchers hope to learn more about the surface interactions so they can further increase the adhesive force. They also want to study the long-term durability of the adhesive, which in a small number of tests became stronger with each attachment. And they may also determine how much adhesive might be necessary to support a human wearing tights and red mask. Because the surfaces may not be uniform, the adhesive force produced by a larger patch may not increase linearly with the size. There is much to learn about the contact between nanotubes and different surfaces.

Low Energy Substrate Technology (LESA)

Advances in low energy substrate adhesive (LESA) technology are helping spur interest in hybrid systems. The materials were developed to bond hybrids and all-plastic structures together without mechanical fasteners. The two-component structural adhesives graft to low energy surfaces and create a sturdy durable bond. And they are suited for materials that can be tough to bond with other types of adhesives. For instance, LESA bonds thermoplastic and thermoset resins, including polypropylene, polyethylene, polystyrene, PTFE, PET, ABS, and others without any surface treatment. It also bonds many thermoplastic-olefin elastomers (TPOs), as well as coated metallic substrates and glass.

Overall adhesive properties and long-term durability make LESA a good candidate for structural bonding of metal/plastic hybrids. For instance, one commercial adhesive performs well at automobile temperatures -40 – 120°C (-40 – 248°F). It has a tensile strength of 22.1 MPa (3250 psi) and, when subjected to extreme loads, the plastic substrate typically fails before the adhesive interface. Environmental weathering does not adversely affect performance. As with other adhesives, LESA can replace or supplement welds and mechanical

**FIGURE 2.6**

The front-end carrier on Volkswagen's new Polo features steel reinforcement bonded to a plastic framework with Betamate low-energy-substrate adhesive from Dow Automotive. The resulting structure reduces weight by 25% compared with previous versions, lowers costs by 10%, and meets structural requirements.

fasteners. It applies and cures at room temperature and requires no extra pressure during curing—the only need is to maintain contact between parts. The benefits of adhesive-bonded hybrid structures has recently been applied in the automobile front-end carrier by Volkswagen, (Figure 2.6). A front-end carrier (FEC) supports most of the cooling system, headlights, hood/trunk latch, and various other components. It connects the upper and lower longitudinal body rails and plays a role in vehicle structural stiffness. Traditional steel FECs are bolted or welded to the body. Adding subcomponents, however, requires welding attachment brackets that increases weight and cost. A recent trend in the automobile industry has been the move to modular systems, which has opened the door to plastics. Molded-plastic FECs consolidate parts as well as reduce weight and cost. However, in most cases, it still takes a hybrid structure of metal and plastic to resist loads on the carrier, particularly in a crash. In traditional hybrid front-end carriers, metal reinforcements attach to the plastic using rivets or heat stakes, or through overmolding. This new solution uses a Dow Automotive adhesive, Betamate, and LESA technology to join the plastic molding and metal reinforcement. The adhesive produces a continuous load-bearing joint between metal and plastic parts, improving stiffness and reducing the high-stress point loads associated with typical mechanical fasteners. It also enables bonding without pretreatment. The assembly technique lets designers use molded box sections, which maintain structural integrity while permitting more cost-effective thermoplastics, such as long-glass, fiber-reinforced polypropylene and thinner wall sections. The FEC bonded with Betamate LESA is now in production in the new Volkswagen Polo in Europe. The Polo's new front end reduces weight by 25%, compared with previous solutions, and meets rigidity demands at reduced cost. The FEC also meets or exceeds requirements for vibration, hood slam, and latch pull under various temperature and environmental conditions. It offers opportunities to integrate components such

as air-intake ducting into the carrier, and facilitates a design that improves pedestrian safety in terms of leg impact.

Hot Melt

A hot melt, solvent-free alternative to the aerosol adhesives commonly used to position and secure reinforcement materials during the vacuum infusion process has been developed. The VAC-TAC adhesive system is designed to hold in place materials such as reinforcement fabrics, core materials, breathers, peel plies, and release films. Some boat builders who use the vacuum infusion process to manufacture one-piece hulls and lower decks have switched from using a traditional aerosol contact adhesive to this new adhesive system. Manufacturers found that they could build the composite structures much faster, saving time and reducing production cost as well as eliminating health and safety issues because the old system depended on the use of a solvent-based contact adhesive.

The VAC-TAC system incorporates a hot melt glue gun, 6 m (.2 ft) of hose, adhesive and toolbox carry case. The adhesive is applied in a hot melt cartridge and the glue gun is connected to an air and electrical supply. The adhesive is melted inside the gun chamber and sprayed directly onto one of the substrates. The materials can be bonded instantly although the adhesive remains sticky for up to 5 minutes, allowing for positioning of the substrates.

Protein

The use of protein-based adhesive materials is being developed for surgical adhesives and implant coatings based on mussels and other marine organism's secretions for adherence to the substrates upon which they reside. Secreted as fluids, these protein adhesives undergo an in-situ cross-linking or hardening reaction leading to the formation of a solid adhesive plaque, which mediates the attachment of the organism to a variety of substrates. By combining key components with a variety of polymers, novel synthetic constructs have been created for both adhesives and antifouling coatings [18].

Epoxy

When you look out your airplane window in a few years, you may not see the familiar rows of rivets. Believe it or not, adhesive bonding has advanced to the point where it can compete with high-performance traditional fastening technologies. Advanced adhesive-bonding technologies are increasingly pulling their weight in high-performance structural assemblies. Besides replacing traditional mechanical fasteners like rivets, nuts and bolts, and screws, they are competing with other bonding techniques like brazing and welding.

Structural adhesives have tensile strengths in the 54.4–74.8 MPa (8000–11,000 psi) range and compressive strengths between 136 and 272 MPa (20,000 to 40,000 psi). Shear stresses act in plane with the two substrates to move them in opposing directions. Most structural adhesives can take 17–23.8 MPa (2500–3500 psi) of shear stress at room temperature. This property is the one most commonly affected by water or chemical attack, so screening tests often take place both with and without water or fluid immersion. Structural epoxies, like Master Bond's EP17HT, can resist moisture, acids, bases, and temperatures up to 316°C (600°F). The epoxy has been used to bond stainless steel bolts to a stainless steel ring that will see 232°C (450°F) service in an acidic environment.

Designers must weigh the stresses the joint will see against assembly considerations to choose the joint best suited to a particular application. The butt joint is the simplest, with two parts bonded end-to-end. Scarf joints are similar, but have the ends of the joining parts beveled at matching angles for more surface area and shear resistance. Lap joints allow even more bonding area, but result in offset surfaces that can be susceptible to peel. This can be resolved with an offset or joggle lap where one part is formed to compensate for the bond line thickness. Machined laps and double laps are other options, but they entail additional manufacturing steps. A strap joint combines the end-to-end butt joint with the greater surface area of a double lap joint.

Anisotropic Conductive Paste (ACP)

For nearly two decades [19], flip-chip technology has been widely used and accepted for several mainstream and high-end applications including flat panel displays and semiconductor modules in the form of chip (die) on glass (COG) and chip (die) on flex (COF). To facilitate the interconnect within these applications, ACFs have generally been the preferred material for several reasons: ACFs offer excellent low contact resistance and compatibility with noble metallization, they have outstanding adhesion to glass and offer highly reliable interconnection on fine resolution lines. But, the higher materials costs of ACFs combined with their multiple step processing requirements and higher cure temperatures make them a less than ideal solution for some of today's lower cost consumer applications.

As the benefits of flip-chip technology have been realized for high-end applications, this process is also finding favor among manufacturers in the consumer products realm. In particular, these devices have proliferated in applications such as radio frequency identification (RFID) and mobile phones. But lower cost consumer electronic products pose different challenges than their high-end counterparts and, therefore, require alternative and more cost-effective materials to facilitate high yield, low-cost production. Particularly in the case of RFID devices, which are found in everything from pet ID tags to department store inventory oversight,

controlling the production cost and enabling extremely high-throughput rates is essential to widespread use of the technology. For RFID assembly and many other low-cost applications, the interconnect adhesive must be less costly than alternative materials, deliver faster throughput, be compatible with lower processing temperatures and provide very good compatibility with nonnoble metals such as etched copper and etched aluminum. Because ACFs don't deliver on these requirements, anisotropic conductive pastes have emerged as the most cost-effective interconnect material for RFID assembly. But, as RFID inlay manufacturers continue to reduce the cost of the tags by using lower cost substrates such as PET or also known as polyester and antennae metallizations like etched aluminum, die cut aluminum, and etched copper, traditional anisotropic conductive paste (ACP) materials aren't offering the robust performance these devices demand. The most common issue with conventional ACPs when used with nonnoble RFID antenna metallizations is that they are prone to galvanic corrosion when subjected to high humidity and high temperature environments.

Because of this, material specialists have developed a newer generation ACP that delivered the known benefits of existing ACP formulations—snap cure capability at low temperature, strong adhesion to etched aluminum and etched copper, long work life at ambient temperature, and a low interconnect contact electric resistance—and extend them to include corrosion resistance. Building on an existing and well-proven Henkel ACP material [19], chemical scientist's applied design of experiment (DOE) methodology to modify the formula, making it corrosion-resistant in humid, higher temperature environments and its rheology more suitable to jet dispensing. Through filler modification and mixture optimization, a robust ACP formulation that addressed all of the needs of modern, low-cost RFID assembly was created and engineered.

The new material, called Acheson CE-3126 [19], not only meets all of the processability requirements of good adhesion strength, snap cure capability, and a long work life, but also has a much improved reliability performance on nonnoble metal substrates as compared to older generation versions. Three materials were evaluated: etched aluminum, etched copper, and vapor deposited copper. In all three cases, the above adhesive's contact joint resistance remained less than 1 ohm after aging in both 85°C (185°F) at 85% relative humidity (RH) up to 168 hours and after 200 thermal shock cycles. The material also offers exceptional process versatility, as it can be screen printed, dispensed, or jetted to address a variety of manufacturing preferences.

RFIDs and other low-cost electronic devices are part of our everyday life—sometimes even unbeknownst to us. The technology that affords our common conveniences must also address consumer-driven cost pressures and RFID specialists, who have turned to lower cost substrate and antenna metallizations now require complementary materials to enable robust assembly, performance, and reliability.

Methacrylate Adhesives

Building a sheet-metal structure? It's likely you might first think of welding when picking an assembly technique. But for some applications, durable adhesives deliver the desired aesthetic.

Tooling Research Inc. (TRI) [20], Walpole, Massachusetts, primarily designs and builds custom electrical, mechanical, and pneumatic equipment and controls as well as machining metal and plastic components. Recently, TRI was tapped to provide outdoor signs for a college campus, the plans called for thin sheets of aluminum to be mounted on a structural framework. The finished sign panels had to be lightweight and removable as well as weather resistant.

Typically, such sheets are welded to a structural backing. But welds distort the sheet metal, leaving divots on the surface. Sign makers must repair the dents with body filler. Filling and smoothing can take several applications and add time and expense to the project. Mechanical fasteners also deform sheet metal. Sheets must be drilled or punched before joining, and installers still have filling and smoothing tasks to perform afterward. Fasteners are also prone to leak or loosen from weather and vandalism.

For the college campus signs, TRI used an adhesive from Devcon, Danvers, Massachusetts. The two-part, 10:1 methacrylate mixes as workers dispense it from manual or pneumatic mixing nozzles. There's no need for a primer, and bonds attain functional cure in an hour at room temperature. Once the adhesive is cured, which takes 24 hours, it can hold 16.6 MPa (2450 psi) in tensile shear using a 0.05 cm (0.02 in.) bond line on grit-blasted substrates. The adhesive spreads loads over the structural framework instead of concentrating them at fastening points. This adds strength. The adhesive also acts to separate substrates electrically, diminishing the likelihood of corrosive electrolysis. The adhesives use 0.076 cm (0.03 in.) diameter glass beads to control bond thickness. "The adhesive works particularly well on panels and thin sections where clean lines and surfaces are the ultimate goal," says TRI President M. Florst.

Keeping that clean look can involve tight tolerances. For this level of precision, TRI uses an adhesive that permits bonds as thin as 0.03 cm (0.01 in.). This Metal Welder I adhesive has a working time of 5–6 minutes, while Metal Welder II sets up in 14–16 minutes. Plastic Welder II has an 18-minute working time. This adhesive, Plastic Welder II, which is a 1:1 two-part mix that cures in 2 hours at room temperature and can join nylon alloys and polyesters, in addition to standard epoxy composites, metals, and wood. It resists UV aging and weathering.

An adhesive's working time is also important when building complex signs. There could be three or four people working at the same time—one gluing, one holding, and one clamping—to complete an assembly before the adhesive sets up.

Some Significant Applications and Future Potential

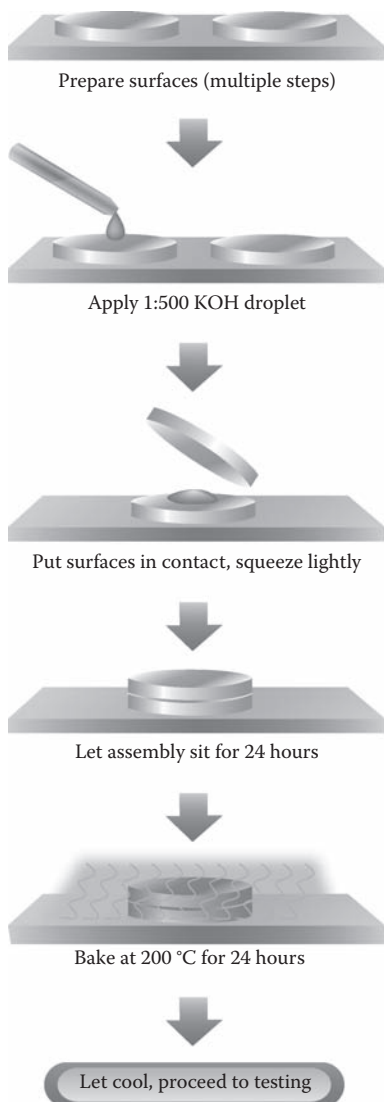
1. Under the U.S. Navy's Surface Strike Affordability Initiative, the Navy Joining Center is leading a project team that is developing an adhesive bonding technology for composite-to-steel structures [21]. While this project is directly supporting the design of the DD(X) multimission destroyer, the technology will have applications for other surface combatant ships including aircraft carriers. The project is being performed by a team with participants from shipyards, aerospace companies, research institutes, and academic universities. The DD(X)s composite deckhouse and helicopter hanger are key components that will help the destroyer to achieve the operational requirements for improved performance, increased survivability, and low ownership cost. These structures take advantage of lightweight, nonmetallic, composite materials to reduce structural weight, ship signature, and in-service maintenance. These new joining techniques are needed to take full advantage of the benefits of composite materials. Currently, mechanical fasteners are used to join composites to steel on navy ships. These fasteners are expensive and their installation procedures are labor intensive. Mechanical fasteners also can become sites for corrosion that often require maintenance during the life of the ship. This project has developed cost-effective adhesive joining technology in response to the DD(X) program's need for improved connections. The joints have been designed to carry both structural and combat loads between major composite and steel ship structures.

Adhesive bonding the composite and steel structures not only eliminates the labor costs associated with mechanical fasteners, but the adhesive-bonded joints have been demonstrated to be 40% lighter and 50% less expensive to produce than the existing bolted joint configuration. The new joints also improve the ship's signature and require less in-service maintenance. Successful designs, analyses, manufacturing development, and testing have resulted in adhesive-bonded joints being selected as the baseline method of attaching the composite deckhouse to the steel hull of the DD(X). This newly developed adhesive bonding technology has already been used to manufacture demonstration articles and test components. The destructive tests of these components have verified the ability of bonded joints to meet or exceed DD(X) design requirements. The project also included development of methods for nondestructive inspection and repair of the joints. These techniques can be applied to both newly manufactured joints as well as joints that have been in service. The vital technology emerging from this effort will serve as a building block for all future composite ship designs and will help meet the needs of the twenty-first-century U.S. Navy.

2. A process for hydroxide-assisted bonding [22] has been developed as a means of joining optical components made of ultra low expansion (ULE) glass, while maintaining sufficiently precise alignment between. The process is intended mainly for use in applications in which (1) bonding of glass optical components by use of epoxy does not enable attainment of the required accuracy and dimensional stability and (2) conventional optical contacting (which affords the required accuracy and stability) does not afford adequate bond strength. The basic concept of hydroxide-assisted bonding is not new. The development of the present process was prompted by two considerations: (1) The expertise in hydroxide-assisted bonding has resided in very few places and the experts have not been willing to reveal the details of their processes and (2) data on the reliability and strength attainable by hydroxide-assisted bonding have been scarce. The first and most critical phase of the present hydroxide-assisted bonding process is the preparation of the surfaces to be bonded. This phase includes the following steps:

- Ultrasonic cleaning in successive baths of acetone, methanol, and propanol, using an ultrasound cleaner that operates at several megahertz.
- Treatment in a solution of potassium hydroxide and ammonium hydroxide in an ultrasonic cleaner, at megahertz frequencies.

Thorough rinsing with deionized water is carried out after each of the above-mentioned steps. The last rinse is followed by ultrasonic cleaning in deionized water, then the cleaned surfaces are blow dried with ionized air. Next, a droplet of a dilute solution of potassium hydroxide is placed on one of the surfaces, then the surfaces are placed in contact and gently squeezed together (see Figure 2.7). The resulting assembly is allowed to sit at room temperature for 24 hours and is then baked at a temperature of 200°C (392°F) for 24 hours. In mechanical tests, sample bonds made by this process were found to have tensile strengths of at least ~9 MPa (1.3 kpsi), where the epoxy bond used to attach the sample to the tensile stress test apparatus broke.3. Scientists have long dreamed about putting telescopes on the far side of the moon where they would be shielded from the interference that affects telescopes on the earth's surface and also in the earth's orbit. One big problem, though, is that the bulk and mass of telescopes make them very expensive to transport to a distant location such as the moon. But researchers at Goddard Space Flight Center in Greenbelt, Maryland, are working on a technique that would make it possible to build a telescope from moon dust and a few common materials that could be transported from Earth. "You can go to the Moon with a few buckets, and build something

**FIGURE 2.7**

Two proposed surfaces are placed in contact with a small amount of a hydroxide solution at the interface. The assembly is allowed to sit and is then baked. The resulting bond is at least as strong as an epoxy bond.

far larger than anything a rocket can carry,” Goddard physicist P. Chen has said.

This work could have an impact on a long-standing debate among astronomers: whether it will be better in the future to build additional orbiting space telescopes such as the Hubble or set them

up on the moon. Both types of telescopes would be beyond the interference and distortions created by the earth's atmosphere, but the moon has the added advantage of being a stable platform with a far side that also would shield a telescope from radio interference from the earth's cluttered radio background. Creating gigantic lunar telescopes would normally carry an astronomical price tag because the earth's gravity places both size and cost limits on what rockets can carry into the earth's orbit, much less a trip to the surface of the moon. To get around that problem NASA researchers used a mix of epoxy, simulated lunar dust, and carbon nanotubes to demonstrate how materials already found on the moon could be used to manufacture a telescope.

Chen has already worked with epoxy and carbon nanotubes to create "smart" materials that can flex or change shape when an electric current passes through, but ended up adding simulated lunar dust, called JSC-1A Coarse Lunar Regolith Simulant, to the mix. Chen used the resulting lunar concrete as the foundation of a 30 cm (11.8 in.) disk and poured more plastic epoxy on top of it. Then he spun the mirror at a constant speed that formed the epoxy into a parabolic, slightly bowl-like shape as it hardened. The mirror's finishing touch came with a thin layer of reflective aluminum applied inside a vacuum chamber.

Making a Hubble-sized mirror would require transporting 60 kg (133.3 lb) of epoxy, 1.3 kg (2.9 lb) of carbon nanotubes and less than 1 gram (0.45 kg) of aluminum to the moon, according to Chen's calculations. Meanwhile, 600 kg (1333 lb) of lunar dust could provide the bulk of the material. The moon's lack of atmosphere also suits the vacuum conditions needed to make the mirror. Astronomers may imagine telescope mirrors half the size of a football field, but realizing such dreams depends heavily on whenever NASA returns human explorers to the moon and sets up a base there. Other challenges include getting the necessary manufacturing equipment to the moon, such as the spinning table on which the mirror gets created. Future astronauts also would have to ensure that none of the free-floating lunar dust contaminates the mirror. "It's a great idea in principle, but nothing is simple on the Moon," J. Spann, a physicist heading the Space and Exploration Research Office at the Marshall Space Flight Center (MSFC), was quoted as saying in an article about the lunar mirror. Spann said the moon's dusty environment would pose challenges, noting that the mirror coating on the earth is done in clean environments. But he also has stated that making simple composite structures has a lot of promise and could be useful for things such as building habitats for lunar bases.

Future efforts by Chen and his colleagues will try to scale up their demonstration by creating 0.5 m (19.68 in.) and 1 m (39.37 in.) mirrors using the simulated lunar dust. They also plan to figure out ways to hone the quality of the finished mirror's surface and are already speculating about ways future explorers and robots could build even larger telescope mirrors on the moon—perhaps within an impact crater.

4. The U.S. Navy Joining Center (NJC) [23] has completed a project to characterize manufacturing variabilities that effect adhesive bonding for composite joints used in the fabrication of primary aircraft structures. The project developed adhesive joint mechanical property data that quantifies the effects of manufacturing variability in adhesive-bonded systems to meet U.S. Navy aircraft service requirements for bonding composite structures. Adhesive bonding of primary aircraft structures has the potential to save significant weight and cost over conventional bonded, riveted, or bolted joint designs with bolts to insure that premature failure will not occur should the bond fail.

As a result of the above-mentioned program, new bonded joint designs have been developed, which minimize peel stresses and provide a more robust joint. The joint, commonly referred to as Pi (P) or a tongue-and-groove joint included a male and female section bonded with an adhesive. This type of joint is more tolerant to damage and flaws than other composite designs. The joints are lighter and less expensive to fabricate than conventional mechanical fastened joints. The target applications of this joint include skin-to-ribbed box composite subassemblies requiring both structural and closeout connections. Even though the Pi-joint configuration has the potential to improve the performance of adhesively bonded joints, fabrication issues were also addressed in the project to insure that the bonded joints can be reproducibly manufactured for primary structure. Large Pi-joint fabrication test elements were manufactured using a range of process variables. Test specimens were produced from the large Pi-joint test elements in sufficient number to provide data on shear loading, combined angle loading, and fatigue performance.

A number of manufacturing variables were identified by airframe manufacturers and tests were performed quantifying their effects on adhesive-bonded joints. Manufacturing variables investigated for adhesive bonding included surface preparation, bond line thickness, offset web, porosity, and impact damage. Results have been released to government agencies as well as industrial aircraft firms [23]. Some of the early data developed in the project was used by designers for bonding of composite

structures in the Joint Strike Fighter (JSF) F-35 program. The application of bonding technology on the inlet duct assembly for the JSF is one example. The results of this project support the U.S. Navy and Air Force requirements for future adhesive-bonded aircraft structures for enhanced performance and operation costs. Cost savings of 60–70% have been realized in assembly operations in bonded structures. As the reliability of adhesive bonding is confirmed, both the Navy and the airframe manufacturers will encourage the use of this joining technology for primary structures.

5. Recently, a new fiber metal laminate (FML) called centrally reinforced aluminum (CentrAl) was introduced for application in aircraft wings [24–27]. The CentrAl concept comprises a central layer of fiber metal laminate (Glare), sandwiched between one or more thick layers of new generation damage tolerant aluminum alloys. The outer layers are also bonded by fiber reinforced adhesive layers, called bondpreg. This creates a robust structural material that is not only exceptionally strong but also insensitive to fatigue. Because the hybrid material is practically immune to fatigue, wing panels can be designed that need no frequent inspection and repair of cracks during the life of the aircraft (i.e., have a “care-free” economic life). The new CentrAl structures are stronger than carbon fiber reinforced plastic (CFRP) structures [24]. CentrAl allows higher stress levels and by using it in lower wing structures, the weight can be reduced by 20% compared to CFRP structures. The application of CentrAl will result in considerably lower manufacturing and maintenance costs.
6. A fast dry adhesive has been used on all FRP components in a new Stark 4-wheel drive vehicle produced by Brazilian vehicle manufacturer, Tecnologia Automotiva Catarinense (TAC). According to Leandro Correia, TAC’s engineer, the need to reduce noise and vibrations was an essential factor in the decision to join FRP components with a fast drying adhesive. Fusor is a two-component polyurethane-based solution from the adhesive manufacturer, Lord Corp., and Lord Corp. was selected to replace the Stark’s mechanical fasteners and act as a substitute for the lamination of the FRP. With an average time for component handling of 30–35 minutes before dryness, the adhesive proved flexible and, according to Correia, improved the vehicles visual style by not using screws and clinches. Future possibilities and applications include replacing the glue currently used on the PP dashboard of the Stark. The Stark is air-conditioned, with a hydraulic wheel, leather seats, electric windows, and a 1.8 VW engine. It is an off-road vehicle designed for muddy and curvy trails.

7. Automaker BMW stepped outside the box when it recently used adhesive-bonded carbon fiber/epoxy roofs to 1500 limited edition BMW M3 CSL sedans. The automaker wanted to enhance the car's performance by shedding as much weight as possible—other composite components include the doors, front skirt, trunk lid, and rear bumper support. The 6 kg (13 lb) carbon roof not only reduces vehicle weight but also lowers its center of gravity, improving stability and handling. Yet, a bonded solution meant that the composite/adhesive combination had to possess stiffness, strength, torsional rigidity, crash impact resistance, and vibration performance equal to a welded steel roof. Manufacturing goals would include ease of application, adequate open time, and a cure time of less than two hours.

BMW conducted extensive adhesive validation studies, including dynamic and static torsion tests, lap shear tests, dynamic mechanical analysis, peel tests, aging/climatic stress tests, and an actual crash test, using different steel paints, surface prep methods, and curing times. While phenolics, epoxies, and acrylics were considered, a two-part polyurethane, PLIOGRIP, manufactured by Ashland Specialty Polymers and Adhesives, Dublin, Ohio, was selected that meets the structural performance requirements for bonds between dissimilar materials at service temperatures of 80°C (176°F), which is the highest temperature the roof will see in hot, sunny weather, yet has sufficient elasticity (~50% elongation) to handle vibration loads.

At installation, the M3 is taken off the production line, workers manually clean the roof with alcohol and water, roughen the mating surfaces, and then hand place a continuous bead of adhesive onto the car's steel roof opening. An assembly jig assists technicians in lowering the roof into place. Pressure is applied with clamps to ensure a tight bond, and "squeeze-out" of excess adhesive is visually confirmed. After a 100 minute room temperature cure, excess adhesive is trimmed and the M3 goes back on line. The adhesives even cure speed, relatively low exotherm, and balance of strength and elasticity were key in its choice: While epoxies may have higher modulus of shear, the polyurethanes have adequate shear to maintain vehicle rigidity—the advantage of higher elasticity is by far the predominant factor.

8. Adhesive tapes, the adhesive resins of which can be cured (and thereby rigidized) by exposure to ultraviolet and/or visible light, are being developed at the Marshall Space Flight Center as repair patch materials. The tapes, including their resin components, consist entirely of solid, low out gassing, nonhazardous or minimally hazardous materials. They can be used in air or in a vacuum and can be cured rapidly, even at temperatures as low as -20°C (-4°F).

Although these tapes were originally intended for use in repairing structures in outer space, they can also be used on Earth for quickly repairing a wide variety of structures. They can be expected to be especially useful in situations in which it is necessary to rigidize tapes after wrapping them around or pressing them into the parts to be repaired.

9. Nanogrip, a Carnegie-Mellon University spin-off [28], has recently been funded to commercialize a fibrous adhesive technology based on the foot hairs of Geckos. The materials mimic the nano- and micro-fibers that provide Geckos and a number of other animals with their ability to grip strongly and repeatedly to smooth and rough surfaces, even in dry and wet outdoor conditions. The goal of this project will assist companies in the design, manufacturing, material selection, and testing of the adhesive for new commercial sportswear applications, in collaboration with leading companies in the sporting goods and materials industries.

References

1. Boëda, E., J. Connan, D. Dessort, S. Muhesen, N. Mercier, H. Valladas, and N. Tisnerat. Bitumen as Hafting Material on Middle Palaeolithic Artefacts, *Nature* 380 (1996): 336–8.
2. Ramanath, G., Rensselaer Polytechnic Institute, Troy, NY, ramanath@rpi.edu; www.rpi.edu; and *AM&P eNews* (August 2007): 24.
3. <http://link.alpi.net/1.php?20080221A2>
4. Li, Y., K. Moon, and C. P. Wong. *Science* 308 (2005): 1419–20.
5. Hwang, J. S. ed. Chapter 1 in *Environment-Friendly Electronics: Lead-Free Technology*, 4–10. Port Erin, UK: Electrochemical Publications, 2001.
6. Li, Y., and C. P. Wong. *Materials Science and Engineering* R51 (2006): 1–35.
7. Lau, J., C. P. Wong, N. C. Lee, S. and W. R. Lee. In *Electronics Manufacturing: With Lead-Free, Halogen-Free, and Conductive-Adhesive Materials*. New York: McGraw-Hill, 2002.
8. Gilleo, K. Chapter 24 in *Environment-Friendly Electronics: Lead-Free Technology*. Edited by J. S. Hwang. Port Erin, UK: Electrochemical Publications, 2001.
9. Li, Y., M. J. Yim, K.-S. Moon, and C. P. Wong. Chapter 11.3 in *Electrically Conductive Adhesives, Smart Materials*, 11.12–11.25. Edited by M. Schwartz. Boca Raton, FL: CRC Press, Taylor & Francis Group, 2009.
10. Dietz, R. L. et al., *Soldering & Surface Mount Technology* 9 (1997): 55.
11. Miragliotta, J., R. C. Benson, T. E. Phillips, and J. A. Emerson. In *Proceedings of the Materials Research Society Symposium* 515 (1998): 245.
12. Cavasin, D., K. Brice-Heans, and A. Arab. In *Proceedings of the 53rd Electronic Components and Technology Conference* (2003): 1404–7.
13. Kisiel, R. *Journal of Electronic Packaging* 124 (2002): 367.

14. de Vries, H., J. van Delft, and K. Slob. IEEE Transactions on Components and Packaging Technologies 28 (2005): 499.
15. Jost, E. M., and K. McNeilly. Proceedings of International Society for Hybrids and Microelectronics Society (1987): 548–53.
16. Lu, D., Q. K. Tong, and C. P. Wong. IEEE Transactions on Components, Packaging and Manufacturing Technology, Part A, 22-23 (1999): 365–71.
17. Mimicking Gecko Feet: Dry Adhesive Based on Carbon Nanotubes Gets Stronger, with Directional Gripping Ability, *Science* October 10, 2008; University of Dayton; Georgia Institute of Technology; AFRL; University of Akron; <http://gtresearchnews.gatech.edu/newsrelease/gecko-fee:10/23/08>.
18. Adhesives from Mussels Combined with Polymers for Implant Coatings, Nerites Corp., 525 Science Drive, University Research Park, Madison, WI, 5371: www.nerites.com
19. Xia, B., J. Shan, and W. O'Hara. *New Corrosion-Resistant Conductive Adhesive for Consumer Applications Delivers Cost-Efficient Alternatives to Current Technologies*, Loctite Industrial Adhesives, Henkel Corp., Rocky Hill, CT.
20. Sign Builder Sticks with Adhesives, *Machine Design* (November 20, 2008): 26–27.
21. Bonded Joint Design Selected for the Baseline for DD(X) Multi-Mission Destroyer, *Welding Journal* (December 2005): 75; and Navy Joining Center (NJC), Columbus, OH (L. Brown, NJC or G. Ritter, EWI).
22. Abramovici, A., and V. White. Hydroxide-Assisted Bonding of Ultra-Low-Expansion Glass, Cal Tech, NASA Jet Propulsion Laboratory, Pasadena, CA and NASA Tech Briefs, April 2008, pp 55–56.
23. NJC Completes Adhesive Bonding Project for Primary Aircraft Structures, NJC and EWI, Columbus, OH (L. Brown, NJC or G. Ritter, EWI).
24. Kwakernaak, A., and J. C. J. Hofstede. Adhesive Bonding: Providing Improved Fatigue Resistance and Damage Tolerance at Lower Costs, *SAMPE Journal* 44, no. 5 (Sept/Oct 2006): 6–15.
25. Bucci, R. J. Advanced Metallic and Hybrid Structural Concepts, *Proceedings USAF Structural Integrity Program Conf. (ASIP 2006)*, San Antonio, TX 2006.
26. Roebroeks, G. H. J. J., P. A. Hooijmeijer, E. J. Kroon, and M. Heinemann. The Development of CentraL, *Proceedings First International Conference on Damage Tolerance of Aircraft Structures*. The Netherlands: TU Delft, 2007.
27. Fredell, R. S., J. W. Funnink, R. J. Bucci, and J. Hinrichsen. “Carefree” Hybrid Wing Structures for Aging USAF Transports, *Proceedings First International Conference on Damage Tolerance of Aircraft Structures*. The Netherlands: TU Delft, 2007.
28. <http://www.compositesworld.com/news/arkema-nanogriptechn-receive-nanomaterial-funding.aspx>: p 1 of 1, 8/11/2009.

Bibliography

Advance High-Performance Epoxy Adhesives Revolutionize Structural Bonding, Master Bond, Inc., 154 Hobart St., Hackensack, NJ 07601.

- Aleksic, S., H. Schweigart, and H. Wack. How Does Cleaning Affect Conformal Coatings, *Zestron America and SMT*, July 13, 2008.
- Bieniak, D., Secrets of Bond Strength, *Machine Design* (July 19, 2008): 60–65.
- Epoxy Adhesives Hold Their Own, *Machine Design* (September 25, 2008): 56–58.
- Fisher, L. W., Better Bonds, *Machine Design* (January 12, 2006): 82–86.
- Hsu, J., NASA Scientists Study Using Moon Dust to Build Telescopes, *Space News* (July 21, 2008): 17.
- Kadioglu, F., M. Es-souni, and S. Hınıslioglu, The Effect of Temperature Increase on the Stress Concentrations of Adhesive Joints, *SAMPE Journal* 37, no. 3 (July 2005): 21–24.
- Naguy, T. A., J. R. Kolek, and T. R. Anderl. *Laser Surface Pretreatment Method for Metal Adhesive Bonding*, AFRL Technology Horizons, 41–42. Dayton, OH: AFRL Materials and Manufacturing, Directorate and Anteon Corp, February 2005.
- Recktenwald, D. Advanced Adhesives Foster Hybrid Structures, *Machine Design* (November 3, 2005): 124–26.
- Rosselli, F. Making the Move From Conventional Joining to Structural Adhesives, *Reinforced Plastics* (February 2006): 42–46.
- Toleno, B. Step 5: Adhesives/Epoxies & Dispensing, *Henkel and SMT*, September 18, 2008.
- Wong, E. W., M. J. Bronikowski, and R. S. Kowalczyk. Using ALD to Bond CNTs to Substrates and Matrices, Cal Tech, NASA Jet Propulsion Laboratory, Pasadena, CA and NASA Tech Briefs, July 2008, pp 50–51.

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Adhesive Proteins from Mussels

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Preface

Mussels, or mollusks, adhere to inanimate and living surfaces in both fresh-water and marine environments. The byssus—an exogenous proteinaceous secretion that enables strong, durable adhesion to many different surfaces in both dry and wet environments—has been the focus of substantial biomaterials development research within the last decade. Understanding the complex mechanisms involved in adhesion by these invertebrates is vital to advancing the formulation and production of mussel-derived bioadhesives. The bio-material development field is actively pursuing the use of various synthetic and naturally derived mussel adhesive proteins for adhesive applications. Potential trends in the adhesives industry, as well as challenges to commercialization of a new field of ecologically friendly adhesives will be discussed.

Background

Marine and freshwater bivalves often use a holdfast termed the byssus to either attach temporarily or permanently in an aqueous environment to a variety of surfaces (Bromley and Heinberg 2005). Individual proteins isolated from mussel byssi have been shown to bond with numerous substrates including glass, Teflon® (E.I. Du Pont de Nemours and Company, Inc., Wilmington, DE, USA) wood, concrete, plastics, metals, biological cell lines, bone, teeth, and others. Mussel byssi contain a mixture of at least 11 proteins that are stockpiled in the foot organ of the animal before being secreted and self-assembled in a process unique in nature. These adhesive-related proteins have been classified as (a) foot proteins (fp): designated fp-1, fp-2, fp-3, fp-4, fp-5, and fp-6; (b) collagens: designated distal collagen (precol-D, furthest from the animal), proximal collagen (precol-P, closest to the animal), and pepsin-resistant nongradient collagen (precol-NG); (c) a proximal thread matrix protein (PTMP-1); and (d) a polyphenol oxidase enzyme. See Table 3.1 for the relationships between these proteins and their materials properties. The adhesive strength of the mussel byssus is determined by the properties of the individual proteins secreted by the animal, the interaction of these proteins with each other, the bonding

TABLE 3.1
Byssal Protein Adhesive and Mechanical Properties

Biological Classification			Adhesive Materials Classification	
Byssus	Region	Mussel Proteins Identified	Function	Curing Mechanism
Plaque	Primer layer	fp-3, fp-5, fp-6	Primer Plaque/primer	Couple with inorganic (i.e., metals) and organics
	Plaque foam	fp-2	Stabilize	Inter- and intramolecular cross-linking
	Thread collagen anchor	fp-4		
Thread	Thread sheath (cuticle)	fp-1	Varnish/coating	Inter- and intramolecular cross-linking
	Thread core	polyphenol oxidase		Oxidation
		distal precol-D	Rigid	Inter- and intramolecular cross-linking
		proximal precol-P, PTMP-1	Elastic Rigid	
		nongradient precol-NG	Rigid and elastic	

of these proteins to substrates, the environmental conditions under which adhesion occurs (e.g., salinity, temperature, pH, season), the biological state of the animal (e.g., age and metabolic state), and the mussel species (Van Winkle 1970; Crisp et al. 1985; Carrington 2002; Holten-Anderson and Waite 2008).

The Mussel Byssus

Freshwater mussels with byssi are found in the subfamily *Dreissena*. They inhabit lakes, ponds, rivers, creeks, canals, and similar habitats. Marine mussels live in intertidal and subtidal areas along coastlines throughout the world, and have also been found in hydrothermal vents and deep seeps on the ocean floor (Nelson and Fisher 1995; MacDonald and Fisher 1996). Mussel byssi from the marine subfamilies *Bathymodiolinae* and *Mytilinae* have been studied extensively and comprise the majority of the fps and collagens studied to date in mussel adhesion. Mussel byssi originate from a root that is attached to the byssal retractor muscle and a stem that extends from the root. Byssal threads terminate into byssal plaques. Figure 3.1 illustrates the anatomy of the common marine mussel, *Mytilus edulis*, also referred to as the “blue mussel” because of its color, or the “bearded mussel” because of the threads produced by the animal.

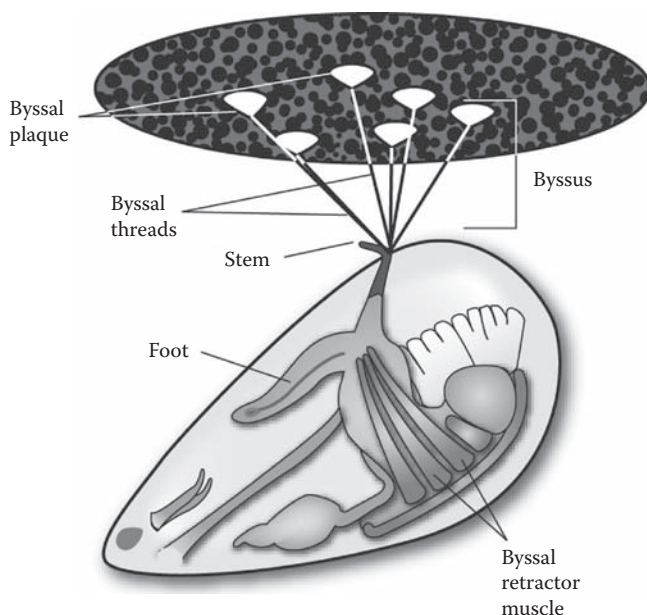


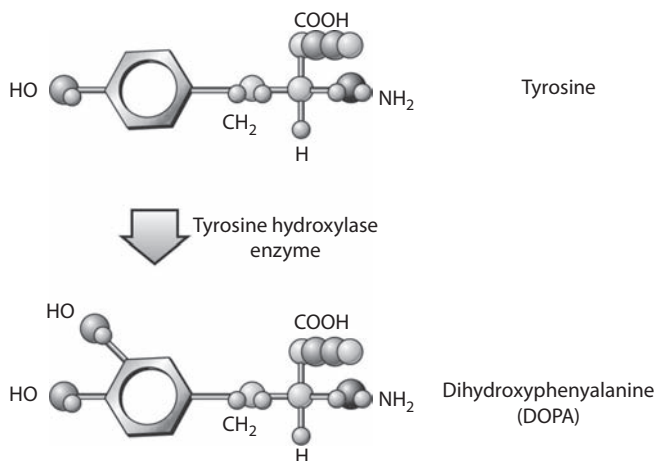
FIGURE 3.1

Anatomy of the common marine mussel, *Mytilus edulis*, also referred to as the “blue mussel” or “bearded mussel.” (From Silverman, H. G. and Roberto, F. F., *Marine Biotechnol.*, 9, 661–8, Figure 3, 2007. With permission from Springer Science+Business Media.)

Adhesive Properties of Byssus Proteins

The first description of the mollusk byssus occurred in 1711 (Brown 1952). Brown’s work nearly 60 years ago noted that byssal threads of *M. edulis* exhibited different morphologies throughout their length, as they emerged from the mussel (proximal thread) and attached to surfaces (distal thread and plaque). Today we know that the distribution of proteins within the thread and plaque are important to the overall mechanical behavior of the threads and their utility to the organism.

As the biochemistry of the byssal thread has been examined, polyphenolic proteins containing 3,4-dihydroxyphenylalanine (DOPA), collagen, and a catechol oxidase that oxidizes tyrosine residues to DOPA (Figure 3.2) have been revealed. DOPA has proven to be a critical chemical contributor to the adhesive properties of proteins making up the byssal thread, and while the exact mechanisms of surface binding and protein cross-linking are still unclear, the ability of this reactive catechol to engage in coordination with metals and metal oxides, form covalent linkages, as well as hydrogen bonds, suggest likely molecular interactions that can be explored and exploited. Repetitive amino acid motifs (fp-1, fp-2), structural amino acid motifs (the collagens), and posttranslational modifications (hydroxylation in fp-1, fp-2, fp-3, fp-5, phosphorylation of fp-5) are additional

**FIGURE 3.2**

Hydroxylation of tyrosine residues in polyphenolic mussel adhesive proteins. (From Silverman, H. G. and Roberto, F. F., *Marine Biotechnol.*, 9, 661–8, Figure 2, 2007. With permission from Springer Science+Business Media.)

biochemical characteristics of the proteins in the byssus (Waite and Tanzer 1981; Rzepecki, Hansen, and Waite 1992; Burzio et al. 1996; Zhao and Waite. 2006a, 2006b, 2006c). The organization of these proteins in the byssal thread, and some of the chemical interactions of DOPA-containing proteins with surfaces and other proteins are shown in Figure 3.3. The importance of metal ions to the polymerization of DOPA-containing byssal proteins was recently demonstrated (Sever et al. 2004), and while ferric iron is clearly important, other metals may also play a role. We discuss additional details of the byssal proteins below.

Byssal Thread Proteins

Byssal threads vary in dimensions (~0.1 mm diameter, 2–4 cm length) and consist of a flexible core encased by a hardened sheath or cuticle. The core contains three unique collagens, precol-P, precol-D, and precol-NG, extending the length of the threads in a gradient fashion (Coyne and Waite 2000; Lucas, Vaccaro, and Waite 2002; Hassenkam et al. 2004). The fp-1 encapsulates the collagens and forms a protective coating after interacting with metals (Sever et al. 2004) and a polyphenol oxidase (Waite and Tanzer 1981).

The Precollagens

Precol-P is ~95 kDa and contains seven separate protein domains: the customary amino and carboxyl termini found in all collagens, and a collagenous domain flanked by two elastin-like domains, which in turn are flanked

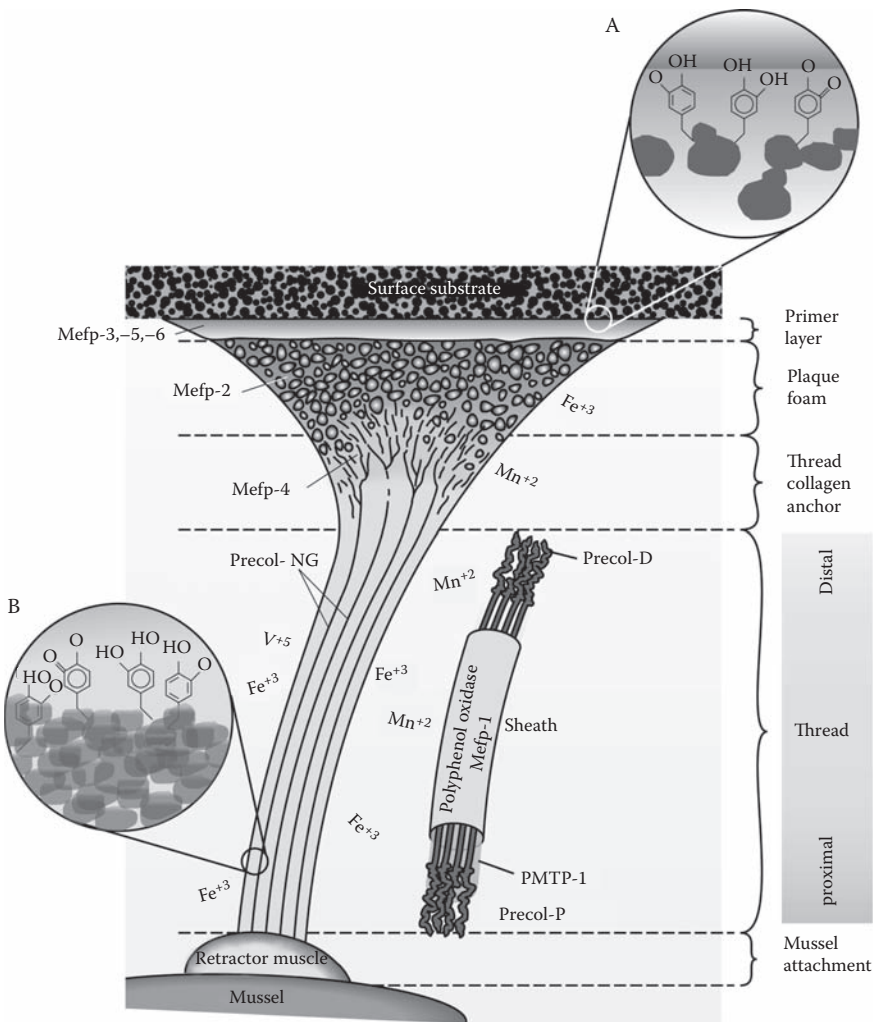


FIGURE 3.3
Organization and location of byssal proteins in the mollusk byssus. Note the gradients of proteins conferring different material properties on the thread between the proximal (adjacent to the mussel) and distal (surface attachment) ends of the thread. These gradients are described in more detail in the text. Inset A depicts the possible role of DOPA-containing proteins fp-3 and fp-5 at the interface between the plaque and the surface, with catecholic and quinone moieties available for interaction with the surface. Inset B interprets/depicts recent information from the Waite laboratory (Adapted from Holten-Andersen, N. and Waite, J. H., *J. Dent. Res.*, 87, 701–9, 2008.) indicating that fp-1 organizes in protein granules to form a protective coating that resists failure in part due to this organization. Fp-1 also contains large amounts of DOPA that is involved in protein cross-linking. (Adapted from Silverman, H. G. and Roberto, F. F., *Marine Biotechnol.*, 9, 661–8, Figure 4, 2007. With permission from Springer Science+Business Media.)

by two histidine-rich domains. Amino acid sequence variants have been observed. The elastic proximal region of the thread is arranged in a coiled configuration, allowing for tough and extensible properties (Qin and Waite 1995; Coyne, Qin, and Waite 1997). Precol-P interacts with metals, suggesting metal-mediated cross-linking may occur (Coyne and Waite 2000). Precol-D is ~97 kDa and also contains seven separate protein domains. Silk fibroin-like domains rather than the elastin-like domains of precol-P flank the central collagenous region, imparting a strong, stiff extensible property to the distal end of the thread (Waite, Qin, and Coyne 1998). The collagenous distal region is configured in straight bundles rather than the coiled nature of precol-P. Precol-NG is ~76 kDa and contains a combination of protein domains found in precol-P and precol-D. It functions as a mediator between these two collagens along the full length of the byssal thread (i.e., nongradient fashion). The protein domains include the amino and carboxyl termini with a larger distribution of tyrosine than the other precols. A central collagenous region is flanked by plant cell wall-like domains, which in turn are flanked by the fibroin-like domains found in precol-D (Qin and Waite 1995).

Foot Protein-1

Fp-1 was the first mussel adhesive protein (MAP) to be identified by J. H. Waite and colleagues (1981, 1983), and has been described in the literature as MAP or *Mytilus edulis* foot protein-1 (Mefp-1). It is ~115 kDa and contains 10–15 mol% DOPA and substantial posttranslational modification of its amino acids. Decapeptide and hexapeptide repeats present in fp-1 contain tyrosine residues that are readily hydroxylated to DOPA and proline residues that are hydroxylated to trans-2,3-*cis*-3,4-dihydroxyproline or trans-4-hydroxy-L-proline. The quinone-tanning reaction (tyrosine to DOPA) is catalyzed by a polyphenol oxidase to form the hardened, protective sheath that surrounds the collagen core. It has recently been shown that these proteins polymerize in granules lend mechanical strength and durability, including an ability to self-heal upon strain, to the sheath (also referred to as the cuticle). Analogous fp-1 sheath proteins appear in many other mussel species, with differences in decapeptide repeat frequencies, amino acid composition and nonrepetitive coding regions [*M. galloprovincialis* (Mgfp-1, Inoue and Odo 1994); *M. coruscus* (Mcfp-1, Inoue et al. 1996b); *M. trossulus* (Inoue et al. 1995b); *M. californianus* Conrad (Waite 1986); *M. chilensis* (Pardo et al. 1990); *M. sp.* JHX-2002 (Wang et al. 2004); *Dreissena polymorpha*, zebra mussel (Dpfp-1, Rzepecki and Waite 1993; Anderson and Waite 2000); *D. bugensis*, quagga mussel (Dbfp-1, Anderson and Waite 2002); *Perna viridis*, green mussel (Pvfp-1, Ohkawa et al. 2004); *P. canaliculus*, green shell mussel (Pcfp-1, Zhao and Waite 2005); *Guekensia demissa*, ribbed mussel (Waite, Hansen, and Little 1989); *Limnoperna fortunei*, Asian freshwater mussel (Lfvp-1, Ohkawa et al. 1999); *Aulacomya ater* (Saez et al. 1991); *Choromytilus chorus* (Pardo et al. 1990)].

Polyphenol Oxidase

A specific polyphenol oxidase (an oxidoreductase) responsible for cross-linking of fp-1 has not been identified. However, catechol oxidase activity has been measured in the foot organ and byssus (Zuccarello 1981; Waite 1985) and nonhomogeneous preparations of enzymes classified as catechol oxidases have been isolated from the mussel foot and regions of the byssus (Burzio 1996; Hellio, Bourgougnon, and Le Gal 2000). Enzyme subunits have ranged from 34 to 174 kDa. Hydroxylation of native (chemically extracted) or synthetically derived fp-1 can be accomplished in vitro with chemical oxidants (e.g., periodate), or enzymatically (mushroom tyrosinase, peroxidase; Marumo and Waite 1986), alkaline environments (pH > 8.5) or dissolved oxygen.

Proximal Thread Matrix Protein

PTMP-1 is a ~50 kDa, water-soluble, noncollagenous protein present in the proximal region of the byssal thread, functioning as a collagen-binding protein and containing amino acid sequences that exhibit a stiffening effect (Sun, Lucas, and Waite 2002). This protein may aid in stabilizing the more flexible precol-P portion of the byssal thread where it attaches to the animal.

Byssal Plaque Proteins

Byssal plaques vary in size, but are usually ~0.15 mm in diameter at the distal end of the byssal thread and ~2–3 mm diameter where they adhere to a substrate (Crisp et al. 1985). Six proteins have been identified in byssal plaques: fp-3, -5, and -6 constitute a region that is believed to function as a primer layer; fp-2 comprises the plaque foam; and fp-4 occupies the thread–plaque junction region between the byssal thread and the byssal plaque. Fp-1 functions as a hardened protective sheath encompassing the plaque—similar to its role in byssal thread formation.

Primer Layer

Fp-3 is ~5–7 kDa and contains 20–25 mol% DOPA as well as 4-hydroxyarginine and tryptophan (Papov et al. 1995; Warner and Waite 1999; Zhou et al. 2006a). Gene families of fp-3 variants have been identified in *M. edulis*, *M. californianus*, and *M. galloprovincialis* with differing conclusions as to why and when the animals secrete specific variants (Inoue et al. 1996a; Florioli, von Langen, and Waite 2000; Zhou et al. 2006a). Fp-5 is ~9.5 kDa and contains 27 mol% DOPA as well as phosphoserine. Fp-5 analogs have been identified in *M. edulis* (Waite and Qin 2001), *M. californianus* (with two variants; Zhao and Waite 2006c), and *M. galloprovincialis* (Hwang et al. 2004).